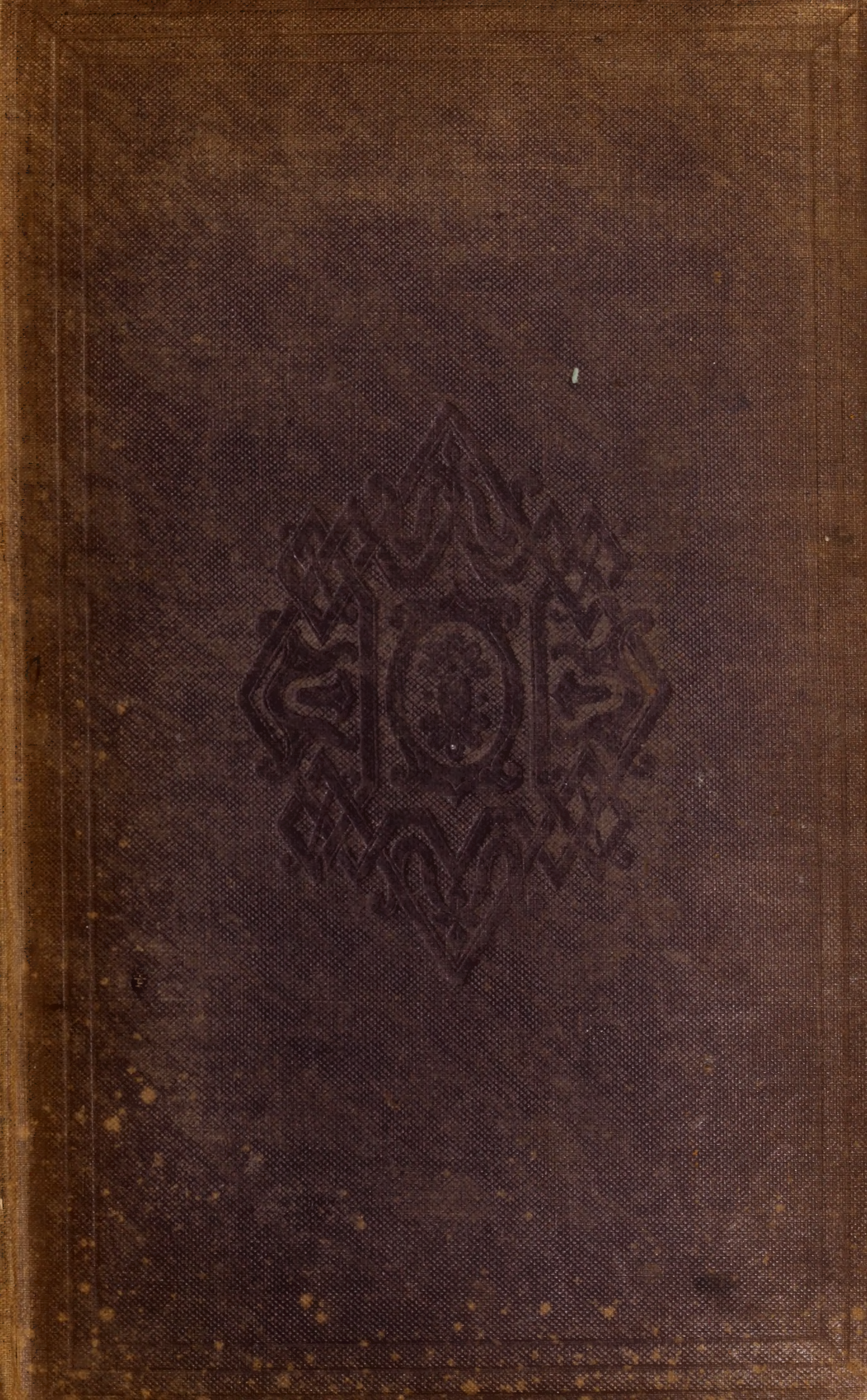

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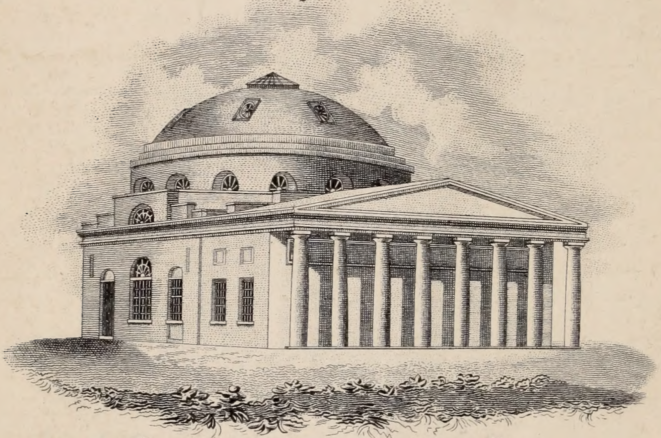

University of Maryland

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April
1856.

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ELEMENTS OF CHEMISTRY,

INCLUDING THE

ACTUAL STATE AND PREVALENT DOCTRINES OF THE SCIENCE.

BY THE LATE

EDWARD TURNER, M.D. F.R.S. L. & E.

EIGHTH EDITION.

EDITED BY

BARON LIEBIG,

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF GIESSEN;

AND

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PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF EDINBURGH.

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PART I.—INORGANIC CHEMISTRY.

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ADVERTISEMENT.

The present Edition of Turner's Elements of Chemistry is formed on the same plan as the last, the Seventh Edition, in which the Editors endeavoured to supply the student with a condensed view of the actual state of the science, more especially of the Organic department, which, in consequence of the rapid progress of discovery, it was necessary in that Edition entirely to re-write.

The favourable reception of that attempt to make the student acquainted with the state and prospects of the science, has rendered it necessary to publish a New Edition ; and in doing so, the Editors, while adhering to the general plan of the last, have introduced all such new facts as appeared to them sufficiently established, and have thus made a very large number of additions and corrections in almost every section.

The present volume contains the whole of the Inorganic Chemistry, and will be speedily followed by the Organic Chemistry, in which the additions and corrections are still more numerous, many sections having been re-written, in order to attain the object in view, namely, an accurate although condensed account of the actual state of the science, of its useful applications, and of its present prospects.

Since the publication of the last Edition, many Continental chemists, including Liebig, Wöhler, Gmelin, and their numerous pupils, have finally adopted the British equivalents or atomic weights for those substances in regard to which a difference existed, as pointed out in the preface to the Seventh Edition. This difference, therefore, no longer exists, as far as concerns the chemists above named, and many others, who, in their works, now admit, as we do, water to be HO, not as formerly H_2O ; and chloride of potassium to be KCl, and not as formerly KCl_2, &c. In short, the atomic weights of Hydrogen, Nitrogen, Chlorine, Bromine, Iodine, and Fluorine are now, by those chemists, assumed to correspond with their equivalents, where formerly the equivalent was made to contain 2 atoms.

It is very gratifying to the Editors, that, anticipating this change on the part of the Continental chemists, they did not, in the last

Edition, confuse the student by any attempt to obtain uniformity; but, as they could perceive no good reason for the system adopted by Berzelius, of making a distinction between equivalents and atoms, (more especially after the discoveries of Dumas and Mitscherlich had shewn that the combining volume of gases could furnish no criterion for the number of atoms forming an equivalent,) waited with confidence for the time when the simple and natural principle adopted in this country should be recognized and adopted on the Continent.

One change has been made in this Edition, that, namely, of doubling the equivalents of Phosphorus, Arsenic, and Antimony, as is now done by most chemists, both here and abroad. The effect of this change is to simplify formulæ, substituting, for example, for such as P_2O_5, As_2O_3, and Sb_2O_3, the more simple formulæ of PO_5, AsO_3, and SbO_3. It seems now to be generally admitted that, in the case of these elements, there is no good reason for using the smaller equivalent, and thus, in all their compounds, assuming 2 eqs. of phosphorus, &c.

In conclusion, it is hoped that the present Edition may be found by the student to supply him with as full and accurate an account of the present state of Chemistry as is possible in a work necessarily limited in size ; and that its imperfections will be ascribed to the vast extent and variety of the topics to be embraced, on most of which new researches are constantly appearing.

WILLIAM GREGORY.

University of Edinburgh,
Oct. 26, 1846.

PREFACE TO THE SEVENTH EDITION.

In offering to the British Public the Seventh Edition of Professor Turner's Elements of Chemistry, the Editor feels it quite unnecessary to advance anything in recommendation of a work so firmly established in the public favour. The death of its lamented Author has thrown into other hands the task of rendering the "Elements of Chemistry" equal to the demands made upon such a treatise by the rapid and unceasing progress of discovery,—of giving, in short, to the student a compendious view of the actual state and prospects of the science.

When the Sixth Edition was projected, in the lifetime of the Author, it was arranged that Professor Liebig should undertake the department of Organic Chemistry, while Dr. Turner himself was to re-write the Inorganic Chemistry, that being the department with which he was more especially familiar. The choice of Professor Liebig has been ratified by the unanimous voice of European chemists, by whom he is admitted to be the first living authority in Organic Chemistry.

The delay which has occurred in the completion of that edition, which is finished along with the present, has been chiefly owing to the wish of Professor Liebig to render it what it professes to be, namely, a durable record of well-established facts. Many laborious series of experiments have been completed in his laboratory with this object alone in view, the results of which are embodied in both editions. This will thus constitute the first tolerably complete account of Organic Chemistry in the English language. In both will be found the latest and most accurate information, as far as it had come into the hands of the English Editor when the respective sheets were written or revised. For examples of the great additional value thus given to the work, the reader is referred to the sections on alcohol and the ethers, on sugar, on benzule, on the vegetable acids; on the oily acids, fixed oils, soaps, and plasters; on the colouring matters and vegetable bases; and, finally, on the azotized products common to the animal and vegetable kingdoms.

Much yet remains to be done, before the boundless field of Organic Chemistry shall be thoroughly explored; but the Editor ventures to entertain the hope, that the present Work, by making the rising generation of British chemists aware of what their brethren on the Continent have done in this department, may contribute to induce them to cultivate Organic Chemistry, and thus secure for their country a share of the honour of those discoveries which will infallibly be made in this division of their science. So rich, indeed, is the vein of discovery in this mine of research, too long neglected among us, that, in the words of Professor Liebig, "we have only to stoop down in order to pick up discoveries from the ground." It need hardly be added, that, to succeed in this, we must proceed on the only true method, the Baconian, that is, rigid induction from facts accurately observed.

The bulk of that part of the work devoted to Organic Chemistry has been of necessity so much increased, that in the present Edition the Editor has been compelled, however reluctantly, to curtail very considerably the sections on Heat, Light, Electricity, and Galvanism, which come more properly, in many of their details, into the province of Physics than into that of Chemistry: the Editor trusts, however, that these subjects will be found as fully treated as is consistent with the character of an Elementary Work on Chemistry.

In the Inorganic Chemistry no material change has been made, except that recently-ascertained facts have been added. The Editor felt that he could not hope to add anything to the beauty and perspicuity of Dr. Turner's exposition of the doctrines of chemistry, and particularly of combination in definite proportions, and of the atomic theory.

One addition has appeared to the Editor indispensable, namely, a sketch of the new views of the constitution of Acids and Salts which at present occupy the attention of chemists. It is yet too early to adopt these views as a principle of arrangement, but the student has a right to expect some account of them. This will be found in the general section on Salts, and also under the head "Theory of Organic Acids." Some remarks on the same subject will also be found under Phosphoric Acid and its modifications. In the opinion of the Editor, the progress of discovery decidedly tends to establish the principal points of the new doctrine; namely, that all acids are composed of radicals, simple or compound, united to hydrogen; that, in salts, metals are substituted for this hydrogen; and, lastly, that there exists a class of acids, to which the term *polybasic* may be applied, which require, to form neutral salts, two, three, or more equivalents of base. On this last point especially a keen controversy, conducted with consummmate talent and praiseworthy moderation on both sides, has been for some time carried on between Dumas and Liebig, the chief advocates of the new views, on the one hand, and Berzelius, the champion of the longer-established doctrine, on the other. As in the case of all scientific controversies, properly conducted, the difference of opinion has led to new researches, the results of which have been highly beneficial to the progress of Chemistry.

The whole of the Organic Chemistry has been re-written and new-modelled, and includes not only the facts most recently ascertained, but also a sketch of those views, both in Vegetable and Animal Chemistry, which have lately been developed by Professor Liebig, and which have excited so great an interest.

In reference to the subject of symbols and formulæ, the Editor, in compliance with the method followed in the Sixth Edition, has adopted the simple and highly useful system recommended by Liebig and Poggendorff. This system is, in his opinion, nearly faultless as a means of condensing the representation of chemical combinations and decompositions into a small space. Its rules are few and easy; and, above all, it is almost universally adopted on the Continent. The Editor has reduced all the formulæ in the work to one system, several having inadvertently been given according to another in the Sixth Edition. All the systems in use, however, are explained, so that the student need have no difficulty in reading any work in which they occur. He would most earnestly recommend to the student early to familiarize himself with the use of symbols and formulæ. The time has now gone by when their utility could be doubted or denied; indeed, it is not too much to say, that the use of formulæ, by facilitating the comprehension of complicated changes, has materially contributed to the progress of chemical discovery. Symbols and formulæ, however, are not to be considered as an attempt to apply mathematics to chemistry; they are simply abbreviations, and, algebraically considered, they include only the use of + and —, in other words, addition and subtraction.

It has not been considered expedient to make any change in the atomic weights usually adopted in England. Unanimity on this point is no doubt highly desirable among chemists of all nations; but the change ought to proceed from some general congress of chemists, and should not be attempted by individuals. The student should bear in mind, in reading foreign works, that the atomic weights of hydrogen, chlorine, bromine, iodine, cyanogen, and nitrogen, adopted on the Continent, are only half as high as those used in England; so that, for example, water with us is represented by HO, while in France and Germany it is H_2O; chloride of potassium, which in England is KCl, on the Continent is KCl_2, and so on.

Finally, the Editor has to apologise for the errors and imperfections of the Work. Those who are best acquainted with the rapid and incessant progress of the science, will be most ready to excuse them; and those who best know its extent, will best appreciate the difficulties which must attend any attempt to compress into One Volume, however large, an accurate or practically useful account of Modern Chemistry.

WILLIAM GREGORY.

King's College, Aberdeen,
October 20*th*, 1842.

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INTRODUCTION.

Material substances are endowed with two kinds of properties, physical and chemical; and the study of the phenomena occasioned by them has given rise to two corresponding branches of knowledge, *Natural Philosophy* and *Chemistry*.

The physical properties are either general or secondary. The general are so called because they are common to all bodies; the secondary, from being observable in some substances only. Among the general may be enumerated extension, impenetrability, mobility, extreme divisibility, gravitation, porosity, and indestructibility.

Extension is the property of occupying a certain portion of space: a substance is said to be *extended* when it possesses length, breadth, and thickness. By *impenetrability* is meant, that no two portions of matter can occupy the same space at the same moment. Every thing that possesses extension and impenetrability is matter.

Matter, though susceptible of *rest and motion*, has no inherent power either of beginning to move when at rest, or of arresting its progress when in motion. Its indifference to either state has been expressed by the term *vis inertiæ*, as if it depended on some peculiar force resident in matter, whereas it arises from matter being absolutely passive, and thereby subject to the influence of every force which is capable of acting upon it.

Matter is *divisible* to an extreme degree of minuteness. A grain of gold may be so extended by hammering that it will cover 50 square inches of surface, and contain two millions of visible points; and the gold which covers the silver wire, used in making gold lace, is spread over a surface twelve times as great. A grain of iron, dissolved in nitro-hydrochloric acid, and mixed with 3137 pints of water, will be diffused through the whole mass: by means of the ferro-cyanuret of potassium, which strikes an uniform blue tint, some portion of iron may be detected in every part of the liquid. The grain of iron is hence inferred to have been divided into rather more than 24 millions of parts; and if the dilution were carried still further, the diffusion of iron through the whole liquid might be proved by concentrating any portion of it by evaporation, and detecting the metal by its appropriate tests.

A keen controversy existed at one time concerning the divisibility of matter, some philosophers affirming it to be infinitely divisible, while others maintained an opposite opinion. Owing to the imperfection of our senses the question cannot be determined by direct experiment, because matter certainly continues to be divisible long after it has ceased to be an object of sense. The decision, if effected at all, can only be accomplished indirectly, as an inference from other phenomena. In favour of the former view it was urged, on mathematical grounds, that a surface admits of division without limit; and that to whatever degree matter is divided, it may still be conceived, as possessing extension and surface, to be susceptible of still further division. Plausible, however, as this mode of reasoning may appear, the opposite opinion is daily becoming more general. It is now commonly believed that matter consists of ultimate particles or molecules, which may indeed be conceived to be divisible, but which by hypothesis are assumed to be infinitely hard and impenetrable, and on that account to be incapable of division. These ultimate particles have received the appellation of *atoms* (from the privative *α* and *τεμνειν* to cut,) as expressive of their nature. The arguments adduced in support of this opinion are principally drawn from the phenomena of chemistry, and from the relations which have been observed to exist between the composition and form of crystallized bodies. These subjects will be considered hereafter: it will now suffice to state, in order to show the nature of the argument, that the supposed existence of atoms accounts for numerous facts, which cannot be satisfactorily explained on any other principle.

All bodies descend in straight lines towards the centre of the earth, when left at liberty at a distance from its surface. The power which produces this effect is termed *gravity, attraction of gravitation*, or *terrestrial attraction;* and the force required to separate a body from the surface of the earth, or prevent it from descending towards it, is called its *weight.* Every particle of matter is equally affected by gravity; and therefore the weight of any body will be proportionate to the number of ponderable particles which it contains.

The minute particles of which bodies consist are disposed in such a manner as to leave certain intervals or spaces between them, and this arrangement is called *porosity.* These interstices may sometimes be seen by the naked eye, and frequently by the aid of glasses; but were they wholly invisible, it would still be certain that they exist. All substances, even the most compact, may be diminished in bulk either by mechanical force or a reduction of temperature. It hence follows that their particles must touch each other at a very few points only, if at all; for if their contact were so perfect as to leave no interstitial spaces, then would it be impossible to diminish the dimensions of a body, because matter is incompressible and cannot yield.—When therefore a body expands, the distance between its particles is increased; and, conversely, when it contracts or diminishes in size, its particles approach each other.

By *indestructibility* is meant, that, according to the present laws of nature, matter never ceases to exist. This statement seems at first view contrary to fact. Water and volatile substances are dissipated by heat, and lost; coals and wood are consumed in the fire, and disappear. But in these and all similar phenomena not a particle of matter is annihilated. The apparent destruction is owing merely to a change of form or composition; for the same material particles, after having undergone any number of such changes, may still be proved to possess the characteristic properties of matter.

The *secondary* properties of matter are opacity, transparency, softness, hardness, elasticity, colour, density, solidity, fluidity, and others of a like nature. Several of these properties, especially those last specified, depend on the relative intensity of two opposite forces—cohesion and repulsion. It is inferred, from the divisibility of matter, that the substance of solids and liquids is made up of an infinity of minute particles adhering together so as to constitute larger masses; and that the mutual adhesion of these particles is owing to a power of reciprocal attraction. This force is called *cohesion*, *cohesive attraction*, or the *attraction of aggregation*, in order to distinguish it from terrestrial attraction. Gravity is exerted between different masses of matter, and acts at sensible and frequently at very great distances; while cohesion exerts its influence only at insensible and infinitely small distances. It enables similar molecules to cohere, and tends to keep them in that condition. It is best exemplified by the force required to separate a hard body, such as iron or marble, into smaller fragments; or by the weight which twine or metallic wire will support without breaking.

The tendency of cohesion is manifestly to bring the ultimate particles of bodies into immediate contact; and such would be the result of its influence, were it not counteracted by an opposing force, a principle of repulsion, which prevents their approximation. It is a general opinion among philosophers, supported by very strong facts, that this repulsion is owing to the agency of heat, which is somehow attached to the elementary molecules of matter, causing them to repel one another. Material substances are therefore subject to the action of two contrary and antagonizing forces, one tending to separate their particles, the other to bring them into closer proximity. The form of bodies, as to solidity and fluidity, is determined by the relative intensity of these powers. Cohesion predominates in solids, in consequence of which their particles are prevented from moving freely on one another. The particles of a fluid, on the contrary, are far less influenced by cohesion, being free to move on each other with very slight friction. Fluids are of two kinds; elastic fluids or aëriform substances, and inelastic fluids or liquids. Cohesion seems wholly wanting in the former; they yield readily to compression, and expand when the pressure is removed; indeed, the space they occupy is chiefly determined by the force which compresses them. The latter, on the contrary, do not yield perceptibly to ordinary degrees of compression, nor does an appreciable dilatation ensue from the removal of pressure, the tendency of repulsion being in them counterbalanced by cohesion.

Matter is subject to another kind of attraction different from those yet mentioned, termed *chemical attraction*, or *affinity*. Like cohesion, it acts only at insensible distances, and thus differs entirely from gravity. It is distinguished from cohesion by being exerted between dissimilar particles only, while the attraction of cohesion unites similar particles. Thus, a piece of marble is an aggregate of smaller portions attached to each other by cohesion, and the parts so attached are called *integrant* particles; each of which, however minute, being as perfect marble as the mass itself. But the integrant particles consist of two substances, lime and carbonic acid, which are different from one another as well as from marble, and are united by chemical attraction. They are the *component* or *constituent* parts of marble. The integrant particles of a body are therefore aggregated together by cohesion; the component parts are united by affinity.

The chemical properties of bodies are owing to affinity, and every chemical phenomenon is produced by the operation of this principle. Though it extends its influence over all substances, yet it affects them in very different degrees, and is subject to peculiar modifications. Of three bodies, A, B, and C, it is often found that B and C evince no affinity for one another, and therefore do not combine; that A, on the contrary, has an affinity for B and C, and can enter into separate combination with each of them; but that A has a greater attraction for C than for B, so that if we bring C in contact with a compound of A and B, A will quit B and unite by preference with C. The union of two substances is called *combination*;

and its result is the formation of a new body endowed with properties peculiar to itself, and different from those of its constituents. The change is frequently attended by the destruction of a previously existing compound, and in that case *decomposition* is said to be effected.

The operation of chemical attraction, as thus explained, lays open a wide and interesting field of inquiry. One may study, for example, the affinity existing between different substances ; an attempt may be made to discover the proportions in which they unite ; and finally, after collecting and arranging an extensive series of insulated facts, general conclusions may be deduced from them. Hence chemistry may be defined the science, the object of which is to examine the relations that affinity establishes between bodies, ascertain with precision the nature and constitution of the compounds it produces, and determine the laws by which its action is regulated.

Material substances are divided by the chemist into simple and compound. He regards those bodies as compound, which may be resolved into two or more kinds of ponderable matter ; those as simple or elementary, which contain but one. The number of the latter amounts, as is now believed, to about sixty ; and of these, agreeably to our present knowledge, all the bodies in the earth consist. The list, a few years ago, was somewhat different from what it is at present ; for the acquisition of improved methods of analysis has enabled chemists to demonstrate that some substances, which were once supposed to be simple, are in reality compound ; and it is probable that a similar fate awaits some of those which are at present regarded as simple.

The composition of a body may be determined in two ways, analytically or synthetically. By analysis, the elements of a compound are separated from one another, as when water is resolved by the agency of galvanism into oxygen and hydrogen ; by synthesis they are made to combine, as when oxygen and hydrogen unite by the electric spark, and generate a portion of water. Each of these kinds of proof is satisfactory ; but when they are conjoined—when water is resolved into its elements, and then reproduced by their union—the evidence is in the highest degree conclusive.

I have followed, in the composition of this treatise, the same general arrangement which I adopt in my lectures. It is divided into four principal parts. The first comprehends an account of the nature and properties of *Heat*, *Light*, and *Electricity*,—agents so diffusive and subtile, that the common attributes of matter cannot be perceived in them. They are altogether destitute of weight ; at least, if they possess any, it cannot be discovered by our most delicate balances, and hence they have received the appellation of *Imponderables*. They cannot be confined and exhibited in a mass like ordinary bodies; they can be collected only through the intervention of other substances. Their title to be considered material is therefore questionable, and the effects produced by them have accordingly been attributed by some to certain motions or affections of common matter. It must be admitted, however, that they appear to be subject to the same powers that act on matter in general, and that some of the laws which have been determined concerning them, are exactly such as might have been anticipated on the supposition of their materiality. It hence follows, that we need only regard them as subtile species of matter, in order that the phenomena to which they give rise may be explained in the language, and according to the principles, which are applied to material substances in general; and I shall therefore consider them as such in my subsequent remarks.

The second part comprises *Inorganic Chemistry.* It includes the doctrine of affinity, and the laws of combination, together with the chemical history of all the elementary principles hitherto discovered, and of those compound bodies which are not the product of organization. Elementary bodies are divided into the non-metallic and metallic; and the substances contained in each division are treated in the order which, it is conceived, will be most convenient for the purposes of teaching. From the important part which oxygen plays in the economy of nature, it is necessary to begin with the description of that principle; and from the tendency it has to unite with other bodies, as well as the importance of the compounds it forms with them, it will be useful, in studying the history of each elementary body, to describe the combinations into which it enters with oxygen gas. The remaining compounds which the non-metallic substances form with each other will next be considered. The description of the individual metals will be accompanied by a history of their combinations, first with the simple non-metallic bodies, and afterwards with each other. The last division of this part will comprise a history of the salts.

The third general division of the work is *Organic Chemistry*, a subject which will be conveniently discussed under two heads, the one comprehending the Chemistry of the compound Radicals, the other treating of the influence of Life on Chemical Products.

The fourth part contains brief directions for the performance of *Analysis.*

ELEMENTS OF CHEMISTRY.

PART I.

IMPONDERABLE SUBSTANCES.

SECTION I.

HEAT, OR CALORIC.

THE term *Heat*, in common language, has two meanings: in the one case, it implies the sensation experienced on touching a hot body; in the other, it expresses the cause of that sensation. When used in the latter sense, it is synonymous with the word *Caloric* (from *Calor*, heat), which is employed exclusively to signify the cause or agent by which all the effects of heat are produced.

Heat, on the supposition of its being material, is a subtile fluid, the particles of which repel each other, and are attracted by all other substances. It is imponderable; that is, it is so exceedingly light, that a body undergoes no appreciable change of weight, either by the addition or abstraction of heat. It is present in all bodies, and cannot be wholly separated from them; for if a substance, however cold, be transferred into an atmosphere which is still colder, a thermometer placed in the body will indicate the escape of heat. That its particles repel one another, is proved by observing that it flies off from a heated body; and that it is attracted by other substances, is inferred from the tendency it has to penetrate their particles, and to be retained by them.

Heat may be transferred from one body to another. Thus, if a cup of mercury at 60° be plunged into hot water, heat passes rapidly from one into the other, until the temperature in both is the same; that is, till a thermometer placed in each stands at the same height. All bodies on the earth are constantly tending to attain an equality, or what is technically called an *equilibrium*, of temperature. If, for example, a number of substances of different temperature be enclosed in an apartment, in which there is no actual source of heat, they will very soon acquire an equilibrium, so that a thermometer will stand at the same point in all. Our varying sensations of heat and cold are owing to a like cause. On touching a hot body, heat passes from it into the hand, and excites the feeling of warmth; when we touch a cold body, heat is communicated to it from the hand, and thus arises the sensation of cold.

Heat is communicated from a hot body to others which are colder in two ways, by *direct contact*, and by *radiation*. By *direct contact*, when the hot body touches a cold one, so that the heat may pass directly from one into the other; as when a bar of iron is put into a fire, or the hand plunged into hot water. By *radiation*, when the heat leaps as it were from a hot to a cold body through an appreciable interval; as when a red-hot ball, suspended in the vacuum of an air-pump, distributes its heat to surrounding objects, or when we are warmed by standing at some distance before a fire. In studying these phenomena we must regard both the loss of heat in the hot body, and the gain of heat in the cold one. The mode in which a hot body cools is, firstly, by giving off heat from its surface either by contact or radiation, or both conjointly; and secondly, by the heat in its interior passing from particle to particle through its substance to its surface. The heating of a cold body is effected, firstly, by heat passing into its surface either by contact or radiation, or by both conjointly; and, secondly, by the heat at its surface passing from particle to particle through its interior portions. Hence, in tracing the laws which regulate the distribution of heat, we shall successively consider the communication of heat from one body to another by *contact*, its passage from particle to particle of the same substance or the *conduction* of heat, and its transfer from a sensible distance or *radiation*.

COMMUNICATION OF HEAT BY CONTACT.

The principal conditions which influence the communication of heat from one body to another by contact are, the degree of contiguity, and the conducting power of the substances. The more perfect the approximation, the more rapid, *cæteris paribus*, is the transfer. The contact of two solids, or of a solid with a gas, is in general of a less perfect kind, and at fewer points, than that between a solid and a liquid; and hence, so far as *contact alone* is concerned, the transfer is more rapid in the latter case than in the former. It is still more rapid when liquids are mixed with each other, or gases with gases, owing to the intermixture of their particles. When bodies touch each other at their surfaces only, the question becomes one of conduction, the rapidity of transfer depending on the velocity with which heat passes through the substances in contact. Thus, if a hot mass of iron and another of marble, of equal size, form, and temperature, be plunged into equal quantities of cold water, the iron will cool faster than the marble, because heat passes more rapidly through the substance of the former than through that of the latter. Were two pieces of hot iron similarly plunged, one into mercury, and the other into water, the piece in contact with mercury would cool most rapidly, because that metal is a better conductor than water. Were the experiment made by immersing the iron into mercury, and the marble into water, the rapidity of cooling in the former would very much exceed that in the latter, from two causes;—both from heat passing more rapidly through iron than through marble, and from its being conveyed away more rapidly by mercury than by water. The same principle explains the unequal sensation caused by bodies of equal temperature. Thus the hand receives a more vivid impression of warmth by touching hot iron than from glass of the same temperature; because the quantity of heat which in a given time can be brought from the interior to the surface of the hot body, so as to pass into the skin, is much greater in iron than in glass. In like manner, cold iron feels colder than glass of the same temperature, because the former conveys away from the skin more heat in a given time than the glass.

CONDUCTION OF HEAT.

By this term is expressed the passage of heat from particle to particle through the substance of bodies. Heat is said to be conducted by them or to pass by *conduction*, and the property on which its transmission depends is termed *conducting power.*

Heat obviously passes through bodies with different degrees of velocity. Some substances oppose very little impediment to its passage, while it is transmitted slowly by others. One cannot leave one end of a rod of iron for some time in the fire, and then touch its other extremity, without danger of being burned, though this may be done with perfect safety with a rod of glass or of wood. The observation of these and similar facts, has led to the division of bodies into *conductors* and *non-conductors* of heat. The former division, of course, includes those bodies, such as the metals, which allow heat to pass freely through their substance; and the latter comprises those which do not give an easy passage to it, such as stones, glass, wood, and charcoal.

Some experiments have been made by Despretz, apparently with great care, on the relative conducting power of the metals and some other substances, and the results are contained in the following table. (An. de Ch. et Ph. xxxvi. 422.)

Gold	1000	Tin	303·9
Silver	973	Lead	179·6
Copper	898·2	Marble	23·6
Platinum	381	Porcelain	12·2
Iron	374·3	Fine clay	11·4
Zinc	363		

An ingenious plan was adopted by Count Rumford (Phil. Trans. 1792,) for ascertaining the relative conducting power of the different materials employed for clothing. He enveloped a thermometer in a glass cylinder blown into a ball at its extremity, and filled the interstices with the substance to be examined. Having heated the apparatus to the same temperature in every instance by immersion in boiling water, he transferred it into melting ice, and observed carefully the number of seconds which elapsed during the passage of the thermometer through 135 degrees. When there was air between the thermometer and cylinder, the cooling took place in 576 seconds; when the interstices were filled with fine lint, it took place in 1032″; with cotton wool in 1046″; with sheep's wool in 1118″; with raw silk in 1284″; with beaver's fur in 1296″; with eider down in 1305″; and with hare's fur in 1315″. The general practice of mankind is therefore fully justified by experiment. In winter, clothing of silk or wool is used in order to retain the animal heat; while in summer, cotton or linen stuffs are preferred, that the heat of the body may the more easily escape.

The conducting power of solid bodies does not seem to be related to any of the other properties of matter; but it approaches nearer to the ratio of their densities than to that of any other property.

Liquids may be said, in one sense, to have the power of conveying heat with great rapidity, though in reality they are very imperfect conductors. This peculiarity is referrible to the mobility which subsists among the particles of all fluids, and to the change of size which is invariably produced by a change of temperature. When any particles of a liquid are heated they expand, thereby becoming specifically lighter than those which have not received an increase of temperature; and if the former happen to be covered by a stratum of the latter, these from their greater density will descend, while the warmer and lighter particles will be pressed upwards. If, therefore, heat enter at the bottom of a vessel containing a liquid, a double set of currents must be immediately established, the one of hot particles rising towards the surface, and the other of colder particles descending to the bottom. These currents take place with such rapidity, that if a thermometer be placed at the bottom, and another at the top of a long jar, the fire being applied below, the upper one will begin to rise almost as soon as the lower. The transport of hot particles by this process has been termed the *convection* of heat.

But if, instead of heating the bottom of the jar, the heat enter by the upper surface, very different phenomena will be observed. The intestine movements cannot then be formed, because the heated particles, from being lighter than those below them, remain constantly at the top: the heat can descend through the fluid only by transmission from particle to particle, a process which takes place so very tardily, as to have induced Count Rumford to deny that water can conduct at all. In this, however, he was mistaken; for the opposite opinion has been successfully supported by Hope, Thomson, and the late Dr. Murray, though they all admit that water, and liquids in general, mercury excepted, possess the power of conducting heat in a very slight degree.

It is extremely difficult to estimate the conducting power of aëriform fluids. Their particles move so freely on each other, that the moment a particle is dilated by heat, it is pressed upwards with great velocity by the descent of colder and heavier particles, so that an ascending and descending current is instantly established. Besides, gaseous bodies allow a passage through them by radiation. Now the quantity of heat which passes by these two channels is so much greater than that which is conducted from particle to particle, that we possess no means of determining their proportion. It is certain, however, that the conducting power of gaseous fluids is exceedingly imperfect, probably even more so than that of liquids.

RADIATION.

When the hand is placed beneath a hot body suspended in the air, a distinct sensation of warmth is perceived, though from a considerable distance. This effect does not arise from the heat being conveyed by means of a hot current; since all the heated particles have an uniform tendency to rise. Neither, for reasons above assigned, can it depend upon the conducting power of the air; because aërial substances possess that power in a very low degree, while the sensation in the present case is excited almost on the instant. There is yet another mode by which heat passes from one body to another; and as it takes place in all gases, and even *in vacuo*, it is inferred that the presence of a medium is not necessary to its passage. This mode of distribution is called *Radiation* of Heat, and the heat so distributed is called *Radiant* or *Radiated Heat.* It appears, therefore, that a heated body suspended in the air cools, or is reduced to an equilibrium with surrounding bodies, in three ways; first, by the conducting power of the air, the influence of which is very trifling; secondly, by the mobility of the air in contact with it; and thirdly, by radiation.

Laws of Distribution.—Heat is emitted from the surface of a hot body equally in all directions, and in right lines, like radii drawn from the centre to the surface of a sphere; so that a thermometer placed at the same distance on any side would stand at the same point, if the effect of the ascending current of hot air could be averted. The calorific rays, thus distributed, pass freely through a vacuum and the air, without being arrested by the latter or in any way affecting its temperature. When they fall upon the surface of a solid or liquid substance they may be disposed of in three different ways:—1, they may rebound from its surface, or be *reflected;* 2, they may be received into its substance, or be *absorbed;* and, 3, they may pass directly through it, or be *transmitted.* In the first and third cases, the temperature of the body on which the rays fall is altogether unaffected; whereas, in the second, it is increased. The heating influence varies with the distance from the radiating body. The rate or law of decrease, as ascertained by careful experiment, and as may be inferred from mathematical considerations, is, that the intensity of heat, like that of light, diminishes in the same ratio as the squares of the distances from the radiating point increase. Thus the thermometer will indicate four times less heat at two inches, nine times less at three inches, and sixteen times less at four inches, than it did when it was only one inch from the heated substance.

The radiation of heat by hot bodies is singularly influenced by the nature and condition of their surfaces, a circumstance which was first examined by Leslie, to whose Essay on Heat, published in 1804, we must still refer for most of our knowledge on this subject. It follows from these researches that velocity of radiation depends more on the *surface* than the *substance* of a radiating body:—that the most imperfect radiators are to be sought among those bodies which are highly smooth and bright, such as polished gold, silver, tin, and brass; but that these same metals radiate freely when their smoothness and polish are destroyed, as by scratching their surfaces with a file, or covering them with whiting or lamp black. A metallic surface seems adverse to radiation independently of its smoothness, since a highly polished piece of glass radiates far better than an equally polished metallic surface. Scratching a surface probably favours radiation by multiplying the number of radiating points.

Some interesting experiments have been made by Dr. Stark of Edinburgh, (Phil. Trans. 1833, Part II.) illustrative of the connection between radiation and the colour of surfaces. The bulb of a delicate thermometer was successively surrounded by equal weights of differently coloured wool, was placed in a glass tube, heated by immersion in hot water to 180°, and then cooled to 50° in cold water. The times of cooling were 21 minutes with black wool, 26 with red wool, and 27 with white wool. Concurring results were obtained with flour of different colours. Likewise, black wool was found to collect more dew than an equal weight of white wool, other circumstances being alike.—This is the first time that direct experiments, seemingly unexceptionable, have been made in proof of the influence of colour over radiation.

Reflection of Heat.—The existence of a reflecting power may be shown by standing at the side of a fire in such a position that the heat cannot reach the face directly, and then placing a plate of tinned iron opposite the grate, and at such an inclination as permits the observer to see in it the reflection of the fire: as soon as it is brought to this inclination, a distinct impression of heat will be perceived upon the face. If a line be drawn from a radiating substance to the point of a plane surface by which its rays are reflected, and a second line from that point to the spot where its heating power is exerted, the angles which these lines form with a line perpendicular to the reflecting plane are called the angles of *incidence* and *reflection*, and are invariably equal to each other. It follows from this law that when a heated body is placed in the focus of a concave parabolic reflector, the diverging rays which strike upon it assume a parallel direction with respect to each other; and that when these parallel rays impinge upon a second concave reflector standing opposite to the former, they are made to converge, so as to meet together in its focus. Their united influence is thus brought to bear upon a single point.

It has been known for ages that the heat contained in the solar rays admits of being reflected by mirrors, and a like property has long since been recognized in the rays emitted by red-hot bodies; but that heat emanates in invisible rays, which are subject to the same laws of reflection as those that are accompanied by light, is a modern discovery, noticed indeed by Lambert, but first decisively established by Saussure and Pictet of Geneva. They first proved it of an iron ball heated so as not to be luminous even in the dark, and then of a vessel of boiling water (Pictet's Essai sur le Feu, p. 65, 1790); but for most of our knowledge of this subject we must again refer to the labours of Leslie. He demonstrated that the reflecting power depends on the nature and condition of surfaces, and that those qualities which are adverse to radiation, are precisely such as promote reflection. Bright smooth metallic surfaces, as polished silver, brass, or tin, which are retentive of their own heat, are little prone to receive heat from other sources, but cause such rays to fly off from them; while those qualities of a surface which facilitate radiation from a hot body, likewise unfit it for reflecting the rays which fall upon it from surrounding objects. His experiments, indeed, justify the conclusion that the faculty of radiation is inversely as that of reflection.

Absorption of Heat.—Every increase of temperature arising from radiant heat is due to its absorption or reception into the body on which it falls. If a pencil of heat impinge on the surface of a body, through which no portion of it is directly transmitted, it must either be absorbed or reflected: those rays which are reflected cannot be absorbed; and those which are not reflected must be absorbed. The number of absorbed rays is supplemental to that of the reflected rays. It hence follows that as the reflecting power is materially influenced by the nature of surfaces, the absorptive power must be so likewise. Those qualities of a surface which increase reflection are to the same extent adverse to absorption; and those which favour absorption are proportionally injurious to reflection. Since, moreover, as was shewn in the last article, the property of radiation is inversely as that of reflection, the power of radiating is directly proportional to that of absorbing heat. These inferences are fully justified by the researches of Leslie, and have received additional confirmation by a decisive experiment made by my colleague, Dr. Ritchie. (Royal Inst. Journal, v. 305.)

The colour of surfaces influences the absorption of radiant heat. This has been observed by several persons of the sun's rays, and of terrestrial heat associated with light, as will be stated in the next section; but the dependence of the absorptive power for simple heat on colour has not till lately been noticed. From researches by Stark already referred to (page 13), it seems that differently coloured wools wound upon the bulb of a thermometer, and exposed within a glass tube to hot water, rose from 50° to 170° in the following times,—black wool in 4′ 30″, dark green in 5′, scarlet in 5′ 30″, white in 8′.

An interesting connection has been traced by Nobili and Meloni between the absorbing and conducting power of surfaces. (An. de Ch. et Ph. xlviii. 198.) In their experiments variations of temperature were estimated by the *thermo-multiplier*, and these researches, if free from fallacy, justify the inference that the radiating and absorbing powers of surfaces for simple heat are in the inverse order of their conducting power.

Transmission of Heat.—Radiant heat passes with perfect freedom through a vacuum. The air and gaseous substances present but a feeble barrier to its progress; so feeble, indeed, that the degree of impediment which they occasion has not yet been appreciated. Most transparent media of a denser kind, on the contrary, such as a diamond, rock crystal, glass, and water, even in thin strata, interfere greatly with its passage. This last remark, however, is only applicable to *simple radiant heat*, that is, to heat unassociated with light. The solar rays pass readily through glass, both heat and light being refracted in their passage, as is shewn by the action of a burning glass or lens; and though much of the heat emitted by the flame of a lamp or a red-hot ball of iron is arrested by glass, many calorific rays are directly transmitted along with the light. But the result is different when the heated body is not luminous. A thin screen of glass interposed between such an object and a thermometer certainly intercepts most of the rays that fall upon it; and the sole question which can be raised is, whether the small effect on the thermometer is caused by direct transmission, or by the screen first becoming warm by absorbing the rays, and then acting by its radiation on the thermometer. On this point the philosophic world was long much divided; but the question has been at length finally set at rest by the masterly researches of Melloni, made with the thermo-multiplier (An. Ch. et Ph. xlviii. 198, liii. 5, lv. 337, lx. 402). He has proved that solids and liquids differ in transmissibility to the rays of heat, just as they differ in their action on light. This may be expressed by the terms *transcalent* and *intranscalent* (*trans* through, *caleo* I heat), or *diathermanous* and *adiathermanous* (δια through, θερμαινω I heat), corresponding to the adjectives transparent and opaque as applied to light. The principal conclusions flowing from his researches are the following:—

1. Though transcalent bodies are also in general more or less transparent, the only known exceptions being opaque black glass and black mica, yet the transcalency and transparency of a substance are not in the same proportion.

2. Radiant heat falling perpendicularly on laminæ of transcalent

bodies having parallel surfaces suffers in all the same degree of reflection, which amounts to 39-1000ths of the incident rays on entering, and 37-1000ths on leaving the lamina.

3. Transcalent bodies differ in the degree of their trancalency. Rock-salt is the only known substance which is perfectly diathermanous: heat from any source falling on a lamina of pure rock salt with parallel faces is not at all absorbed, all the rays which are not reflected being directly transmitted; and this is true whether the laminæ be thick or thin. The result is different with other transcalent bodies, which always absorb a portion of the incident rays. Of 100 rays of heat from the same source successively incident on laminæ of equal thickness of rock-salt, alum, flint-glass, and crown-glass, the transmitted rays were 92, 12, 65, and 49. Of 100 rays similarly incident on strata of water, chloride of sulphur, bisulphuret of carbon, ether, and alcohol, the transmitted rays were 11, 63, 63, 21, and 15. The rays transmitted through similar laminæ of coloured glass were 53 per cent. with violet glass, 47 with red, 34 with yellow, 33 with blue, and 26 with green glass.

4. In glass and liquids those are most transcalent which have the greatest refractive power in regard to light. This is shown in No. 3, where only 11 per cent. of the incident heat passed through water, and 63 through a similar stratum of bisulphuret of carbon. But the law is not applicable to crystalline bodies: thus, as above, 92 per cent. of the incident rays find their way through rock salt, and 12 per cent. through a similar stratum of alum; while their refractive powers for light are nearly the same.

5. The quantity of radiant heat transmissible through glass varies with the temperature of the source from which the rays emanate. Of 100 rays successively incident on the same lamina of glass from the four sources, an oil-lamp, red-hot platinum, blackened copper heated to 734°, and the same copper at 212°, the number of rays transmitted were 77, 57, 34, and 12. Similar results were formerly obtained by De la Roche (Biot's Traité de Physique, iv. 638); and Melloni has proved that diathermanous bodies in general act in the same manner as glass. The only exception is rock-salt, which is equally permeable to rays from sources of as low as of a high temperature. It further appears that rays from the same source pass through some media more readily than through others. It seems an unavoidable inference from Melloni's experiments, that radiant heat has different properties according to its source; that there are various kinds or states of radiant heat, just as there are various kinds or states of light as manifested by its different colours. The rays of light which have passed through

blue glass will pass through a second blue glass more easily than through glass of a different colour, though otherwise less opaque than the blue glass. So do calorific rays, after transmission through water, pass through a second stratum of water more readily than through liquids otherwise more diathermanous, such as alcohol or ether. The water absorbs many rays which might have had the power to pass through alcohol, and gives passage to others which can penetrate water, but not alcohol. Hence it should follow, as Melloni has proved, that comparatively little heat is absorbed by multiplying screens of the same material, or increasing the thickness of one screen : it is the first screen, or the side of one screen, next the radiating substance, by which the principal absorption of heat is effected. The quantity of heat arrested by increasing the thickness of a screen decreases in a very rapid ratio. These facts establish between heat and light new and deeply interesting relations, which will be referred to in the next section.

6. Melloni has established the refrangibility of heat by diathermanous media. Prior observers failed of obtaining decisive evidence of this property, in consequence of using prisms or lenses of glass, the feeble transcalency of which unfits it for such an inquiry ; but with a prism of rock-salt Melloni easily demonstrated the general principle, and proved that heat from different sources, like light of different colours, has different degrees of refrangibility.

Polarization and double Refraction of Heat.—These properties of radiant heat, which Melloni with all his skill vainly attempted to demonstrate, have lately been established in regard to heat, both from luminous and non-luminous sources, by Forbes,—a discovery of great interest, as drawing still closer the relations of heat and light, and for which he has received the well-merited honour of the Keith medal, awarded by the Royal Society of Edinburgh. Forbes has polarized heat by all the methods which polarize light,—by reflection, refraction, and double refraction. He also depolarized heat ; and as this occurs only as a consequence of double refraction, he thereby proved the double refraction of heat. The instrument used by Forbes was the thermo-multiplier, brought to such extreme delicacy that it is supposed sensible to 1-1500th of a degree of Fahrenheit's thermometer. (Phil. Trans. Ed. 1835.)

Theory of Radiation.—The tendency which all bodies evince to attain an equality of temperature by means of radiation, has given rise to two ingenious theories, suggested respectively by Pictet and Prevost. According to the former, bodies of equal temperature do not radiate at all ; and when the temperature is unequal, the hotter give calorific rays to the colder bodies till an equilibrium is established, at which moment the radiation ceases. Prevost, on the contrary, conceived radiation to go on at all times, and from all substances, whether their temperature were the same or different from that of surrounding objects (Recherches sur la Chaleur). Consistently with this view, the temperature of a body falls whenever it radiates more heat than it absorbs; its temperature is stationary when the quantities emitted and received are equal; and it grows warm when the absorption exceeds the radiation. Of these theories the preference is very generally accorded to the latter.

Adopting, then, the theory of Prevost, it will be useful to examine a few instances of its application;—and, first, in regard to the experiments with conjugate mirrors. If a metallic ball in the focus of one mirror, and a thermometer in that of the other, be of the same temperature as the surrounding objects (say at 60°), the thermometer will remain stationary. It will indeed receive rays from the ball; but as it emits an equal number in return, its temperature will be unchanged. If the ball is above 60° the thermometer will rise, because it then receives a greater number of rays than it emits. If, on the contrary, the ball is below 60°, the thermometer, being the warmer of the two bodies, emits more rays than it receives, and its temperature will fall.

The same mode of reasoning explains an interesting experiment originally performed by the Florentine Academicians, and since carefully repeated by Pictet. He placed a piece of ice instead of the metallic ball in the focus of his mirror, and observed that the thermometer in the opposite focus immediately descended, but rose again as soon as the ice was removed. On replacing the ice in the focus, the thermometer again fell, and reascended when it was withdrawn. It was supposed by some philosophers that this experiment proved the existence of frigorific rays, endowed with the property of communicating coldness; whereas, all the preceding remarks were made on the supposition that cold is merely a negative quality arising from the diminution of heat. Nor is the foregoing experiment inconsistent with such an opinion: on the contrary, it is readily accounted for by the theory of Prevost, and might have been anticipated by its application. The thermometer, in fact, has its temperature lowered, because it emits more rays than it receives; and it rises when the ice is removed, because it then receives a number of calorific rays radiated by the warmer surrounding objects, which were intercepted by the ice while it was in the focus.

An elegant application of this theory was made by Dr. Wells to account for the formation of dew. The most copious deposit of dew takes place when the weather is clear and serene; and the substances that are covered with it are always colder than the contiguous strata of air, or than those bodies on which dew is not deposited. In fact, dew is a deposition of water previously existing in the air as vapour, and which loses its gaseous form only in consequence of being chilled by contact with colder bodies. In speculating, therefore, about the cause of this phenomena, the chief object is to discover the cause of the reduction of temperature. The explanation proposed by Wells, in his excellent Treatise on Dew, and now universally adopted, is founded on the theory of Prevost. If it be admitted that bodies radiate at all times, their temperature can remain stationary only by their receiving from surrounding objects as many rays as they emit; and should a substance be so situated that its own radiation may continue uninterruptedly without an equivalent being returned to it, its temperature must necessarily fall. Such is believed to be the condition of the ground in a calm starlight evening. The calorific rays which are then emitted by substances on the surface of the earth, are dispersed through free space and lost: nothing is present in the atmosphere to exchange rays with them, and their temperature consequently diminishes. If, on the contrary, the weather be cloudy, the radiant heat proceeding from the earth is intercepted by the clouds, an interchange is established, and the ground retains nearly, if not quite, the same temperature as the adjacent portions of air.

All the facts hitherto observed concerning the formation of dew, tend to confirm this explanation. Dew is deposited sparingly or not at all in cloudy weather; all circumstances which promote free radiation are favourable to its deposition; good radiators of heat, such as grass, wood, the leaves of plants, and filamentous substances in general, reduce their temperature, in favourable states of the weather, to an extent of 10, 12, or even 15 degrees below that of the circumambient air; and while these are drenched with dew, pieces of polished metal, smooth stones, and other imperfect radiators, are barely moistened, and are nearly as warm as the air in their vicinity.

Cooling of Bodies. — Heated bodies cool by two very different methods. When a hot body is enveloped in solid substances, its heat is withdrawn solely by communication, and the velocity of cooling depends on the conducting power. Cooling is effected in a similar manner when the heated body is immersed in a liquid; but the velocity of cooling then depends partly on the conducting power of the liquid, and partly on the mobility of its particles. In elastic fluids the cooling takes place both by communication and radiation; and in a vacuum it is produced solely by radiation.

EFFECTS OF HEAT.

The phenomena that may be ascribed to this agent, and which may therefore be enumerated as its effects, are numerous. With respect to animals, it is the cause of the feelings of cold, agreeable warmth, and burning, according to its intensity. It excites the system powerfully, and without a certain degree of it the vital actions entirely cease. Over the vegetable world its influence is obvious to every eye. By its stimulus co-operating with air and moisture, the seed bursts its envelope and yields a new plant, the buds open, the leaves expand, and the fruit arrives at maturity. With the declining temperature of the seasons the circulation of the sap ceases, and the plant remains torpid till it is again excited by the stimulus of heat.

The dimensions of every kind of matter are regulated by this principle. Its increase, with few exceptions, separates the particles of bodies to a greater distance from each other, producing expansion, so that the same quantity of matter is thus made to occupy a larger space; and the diminution of heat has an opposite effect. Were the repulsion occasioned by this agent to cease entirely, the atoms of bodies would come into actual contact.

The form of bodies is dependent on heat. By its increase solids are converted into liquids, and liquids are dissipated in vapour; by its decrease vapours are condensed into liquids, and these become solid. If matter ceased to be under the influence of heat, all liquids, vapours, and doubtless even gases, would become permanently solid; and all motion on the surface of the earth would be arrested.

When heat is accumulated to a certain extent in bodies, they shine or become *incandescent*. On this important property depend all our methods of artificial illumination.

Heat exerts a powerful influence over chemical phenomena. There is, indeed, scarcely any chemical action which is not in some degree modified by this principle; and hence a knowledge of its laws is indispensable to the chemist. By its means bodies previously separate are made to combine, and the elements of compounds are disunited. An undue proportion of it is destructive to all organic and many mineral compounds; and it is essentially concerned in combustion, a process so necessary to the wants and comforts of man.

Of the various effects of heat above enumerated, several will be discussed in other parts of the work. In this place it is proposed to treat only of its influence over the dimensions and form of bodies, a subject which will be conveniently studied under the three heads of expansion, liquefaction, and vaporization.

EXPANSION.

One of the most remarkable properties of heat is the repulsion which exists among its particles, a property which enables it, on entering into a body, to remove the integral molecules of the substance to a greater distance from each other. The body, therefore, becomes less compact than before, occupies a greater space, or in other words, expands. This effect of heat is opposed to cohesion—that force which tends to make the particles of matter approximate, and which must be overcome before any expansion can ensue. Heat, therefore, should produce the greatest expansion in those bodies which are least influenced by cohesion, an inference fully justified by observation. Thus the force of cohesion is greatest in solids, less in liquids, and least of all in aëriform substances, while the expansion of solids is trifling, that of liquids much more considerable, and that of elastic fluids far greater.

It may be laid down as a rule, the reason of which will now be obvious, that all bodies are expanded by heat, and that the expansion of the same body increases with the quantity of heat which enters it. But this law does not apply, unless the form and chemical constitution of the body is preserved. For if a change in either be occasioned, then the reverse of expansion may ensue; not, however, as the direct consequence of an augmented temperature, but as the result of a change in form or composition.

To prove the expansion of solids, we need only take the exact dimensions in length, breadth, and thickness, of any substance when cold, and measure it again while strongly heated, when it will be found to have increased in every direction. This dilatation from heat and consequent contraction in cooling take place with a force which appears to be irresistible.

The expansion of solids has engaged the attention of several experimenters, who have endeavoured to determine the exact quantity by which different substances are lengthened by a given increase of heat, and whether or not their elongation is equable at different temporatures. Their expansion, for example, from the freezing point of water to 122°, is equal to what takes place betwixt 122° and 212°. The researches of Dulong and Petit (An. de. C. et P. vii.) prove that solids do not dilate uniformly at high temperatures, but expand in an increasing ratio; that is, the higher the temperature beyond 212°, the greater the expansion for equal additions of heat. It is manifest, indeed, from their experiments, that the rate of expansion is an increasing one even between 32 and 212; but the differences which exist within this small range are so inconsiderable as to escape observation, and for most practical purposes may be disregarded.

The subjoined table includes the most interesting results of Lavoisier and Laplace, who have carefully investigated the linear expansion of solids. (Biot, i. 158.)

Names of Substances.	Elongation when heated from 32° to 212°.
Glass tube without lead, a mean of three specimens	$\frac{1}{1115}$ of its length.
English flint glass	$\frac{1}{1248}$
Copper	$\frac{1}{581}$
Brass—mean of two specimens	$\frac{1}{532}$
Soft iron forged	$\frac{1}{819}$
Iron wire	$\frac{1}{812}$
Untempered steel	$\frac{1}{927}$
Tempered steel	$\frac{1}{807}$
Lead	$\frac{1}{351}$
Tin of India	$\frac{1}{516}$
Tin of Falmouth	$\frac{1}{462}$
Silver	$\frac{1}{524}$
Gold—mean of three specimens	$\frac{1}{602}$
Platinum, determined by Borda	$\frac{1}{1167}$

Knowing the elongation of any substance for a given number of degrees of the thermometer, its total increase in bulk may in general be calculated by trebling the number which expresses its increase in length.

The expansion of liquids is proved by putting a common thermometer, made with mercury or alcohol, into warm water, when the dilatation of the liquid will be shown by its ascent in the stem. The experiment is indeed illustrative of two other facts. It proves, first, that the dilatation increases with the temperature; for if the thermometer be plunged into several portions of water heated to different degrees, the ascent will be greatest in the hottest water, and least in the coolest portions. It demonstrates, secondly, that liquids expand more than solids. The glass bulb of the thermometer is itself expanded by the hot water, and therefore is enabled to contain more mercury than before; but the mercury being dilated to a much greater extent, not only occupies the additional space in the bulb, but likewise rises in the stem. Its ascent marks the difference between its own dilatation and that of the glass, and is only the apparent, not the actual, expansion of the liquid.

Different liquids do not expand to the same degree from an equal increase of temperature. Alcohol expands much more than water, and water than mercury. From the frequency with which the latter is employed in philosophical experiments, it is important to know the exact amount of its expansion. This subject has been investigated by several philosophers, but the experiments of Lavoisier and Laplace, and especially of Dulong and Petit, from the extreme care with which they were made, are entitled to the greatest confidence. According to the former the actual dilatation of mercury, in passing from the freezing to the boiling point of water, amounts to $\frac{100}{5412}$ of its volume; but the result obtained by Dulong and Petit, who found it $\frac{100}{5550}$, is probably still near the truth. Adopting the last estimate, this metal dilates, for every degree of Fahrenheit's thermometer, $\frac{1}{1990}$ of the bulk which it occupied at the temperature of 32°. The apparent expansion of mercury contained in glass is of course less than the absolute expansion. Between the limits of 32° and 212° Lavoisier and Laplace estimate the apparent expansion at $\frac{1}{63}$, and Dulong and Petit at $\frac{1}{64{\cdot}8}$ of its volume, being $\frac{1}{11664}$ for each degree of Fahrenheit's thermometer.

All experimenters agree that liquids expand in an increasing ratio, or that equal increments of heat cause a greater dilatation at high than at low temperatures. Thus if a fluid is heated from 32° to 122° it will not expand so much as it would do in being heated from 122° to 212°, though an equal number of degrees is added in both cases. In mercury the first expansion, according to Deluc, is to the second as 14 to 15; in olive oil as 13·4 to 15; in alcohol as 10·9 to 15; and in pure water 4·7 to 15.

There is a peculiarity in the effect of heat upon the bulk of some fluids; namely, that at a certain temperature increase of heat causes them to contract, and its diminution makes them expand. This singular exception to the general effect of heat is only observable in those liquids which increase in bulk in passing from the liquid to the solid state, and is remarked only within a few degrees of temperature above their point of congelation. Water is a noted example of it. Ice swims upon the surface of water, and therefore must be lighter than it; a convincing proof that water in the act of freezing must expand. The specific gravity of ice is nearly 0·92, which gives the volume of ice to that of water as 1 to 0·92; that is, water expands by about 1-11th of its volume in passing into ice.

But it is not only during the act of congelation that water expands; since it begins to dilate some time before it actually freezes. Dr. Croune noticed this phenomenon so early as the year 1683, and it has since been observed by various philosophers. To render this obvious, fill a flask, capable of holding three or four ounces, with water at the temperature of 60°, and adapt to it a cork, through which passes a glass tube open at both ends, about the eighth of an inch wide, and ten inches long. After having filled the flask, insert the cork and tube, and pour a little water into the latter till the liquid rises to the middle of it. On immersing the flask into a mixture of pounded ice and salt, the water at first contracts, and therefore descends in the tube; but soon after an opposite movement ensues, indicating dilatation, though the water within the flask is at the same time yielding heat to the freezing mixture in which it is immersed.

To the inference deduced from this experiment it was objected, that the ascent of the water in the tube is not referrible to expansion in the liquid, but to contraction of the flask, diminishing its capacity. In fact, this cause does operate, though not to a degree sufficient to account for the whole effect; and, accordingly, it has been proved by an elegant and decisive experiment of Dr. Hope, that water does really expand previous to congelation. He believed the greatest density of water to be between 39·5° 40°; that is, boiling water obeys the usual law till it has cooled to the temperature of about 40°, after which the abstraction of heat produces increase instead of decrease of volume (Phil. Trans. Ed. v. 379). Hallström, who has examined this point with much care, estimates it at 39°.

The cause of the expansion of water at the moment of freezing is attributed to a new and peculiar arrangement of its particles. Ice is in reality crystalized water, and during its formation the particles arrange themselves in ranks and lines, which cross each other at angles of 60° and 120°, and consequently occupy more space than when liquid. This may be seen by examining the surface of water while freezing in a saucer.

Water is not the only liquid which expands under reduction of temperature, as the same effect has been observed in a few others which assume a highly crystalline structure on becoming solid;—fused iron, antimony, zinc, and bismuth, are examples of it. Mercury is a remarkable instance of the reverse; for when it freezes, it suffers a very great contraction.

As the particles of air and aëriform substances are not held together by cohesion, it follows that increase of temperature must occasion a considerable dilatation of them; and, accordingly, they are found to dilate from equal additions of heat much more than solids or liquids.

This subject had been unsuccessfully investigated by several philosophers, who failed in their object chiefly because they neglected the precaution of drying the gases upon which they operated; but at last the law of dilatation was detected by Dalton and Gay-Lussac nearly at the same time.

It is proved by the researches of these philosophers, that all gases undergo equal expansions by the same addition of heat, supposing them placed under the same circumstances; so that it is sufficient to ascertain the law of expansion observed by any one gas, in order to know the law for all. The experiments of Gay-Lussac show that 100 parts of air in being heated from 32° to 212° expand to 137·5 parts. The increase for 180 degrees is therefore 0·375 or $\frac{37{\cdot}5}{100}$ths of its bulk; and by dividing this number by 180, it is found that a given quantity of dry air dilates to $\frac{1}{480}$th of the volume it occupied at 32°, for every degree of Fahrenheit's thermometer. The result of Dalton's experiments corresponds very nearly with the foregoing.

This point being established, it is easy to ascertain what volume any given quantity of gas should occupy at any given temperature. Suppose a certain portion of gas to occupy 20 measures of a graduated tube at 32°, it may be desirable to determine what would be its bulk at 42°. For every degree of heat it has increased by $\frac{1}{480}$th of its original volume, and therefore, since the increase amounts to ten degrees, the 20 measures will have dilated by $\frac{10}{480}$ths. The expression will therefore be $20 + 20 \times \frac{10}{480} = 20{\cdot}416$. The volume which the gas occupies at 32° is a necessary element in all such calculations. Thus, having 20·416 measures of gas at 42°, the corresponding bulk for 52° cannot be calculated by the formula $20{\cdot}416 + 20{\cdot}416\frac{10}{480}$; the real expression is $20{\cdot}416 + 20\frac{10}{480}$, because the increase is only $\frac{10}{480}$ths of the space occupied at 32°, which is 20 measures. A similar remark applies to the formula for estimating the effect of heat on the height of the barometer.

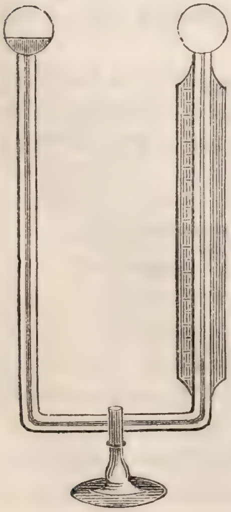
The rate of expansion of atmospheric air at temperatures exceeding 212° has been examined by Dulong and Petit, and the following table contains the result of their observations. (An. de Ch. et Ph. vii. 120.)

Temperature by the Mercurial Thermometer.		Corresponding volumes of a given volume of air.
Fahrenheit.	Centigrade.	
— 33	— 36..	0.8650
32	0..	1.0000
212	100..	1.3750
302	150..	1.5576
392	200..	1.7389
482	250..	1.9189
572	300..	2.0976
M. boils 680	360..	2.3125

Hydrogen gas was found to expand in the same proportion, so that all gases may be inferred to expand to the same extent, for equal increments of heat, between—33° and 680°; and the same law probably prevails at all temperatures.

ON THE THERMOMETER.

The influence of heat over the bulk of bodies is better fitted for estimating a change in the quantity of that agent than any other of its properties; for substances not only expand more and more as the temperature increases, but in general return exactly to their original volume when the heat is withdrawn. The first attempt to measure the intensity of heat on this principle was made early in the seventeenth century, and the honour of the invention is by some bestowed on Sanctorius, by others on Cornelius Drebel, and by others on the celebrated Galileo. The material used by Sanctorius was atmospheric air. There are, however, two forcible objections to the general employment of this thermometer. In the first place, its dilatations and contractions are so great, that it is inconvenient to measure them when the change of temperature is considerable; and, secondly, its movements are influenced by pressure as well as by heat, so that the instrument would be affected by variations of the barometer, though the temperature should be quite stationary.



For the reasons just stated, the common air thermometer is rarely employed; but a modification of it, described in 1804 by Leslie in his Essay on Heat under the name of *Differential Thermometer*, is entirely free from the last objection, and is admirably fitted for some special purposes. This instrument was invented a century and a half ago by Sturmius, Professor of Mathematics at Altdorff, who has left a description and sketch of it in his *Collegium Curiosum*, p. 54, published in the year 1676; but like other air thermometers it had fallen into disuse, till it was again brought into notice by Leslie. As now made it consists of two thin glass balls joined together by a tube, bent twice at a right angle, as represented in the annexed figure. Both balls contain air, but the greater part of the tube is filled with sulphuric acid coloured with carmine. It is obvious that this instrument cannot be affected by any change of temperature acting equally on both balls; for as long as the air within them expands or contracts to the same extent, the pressure on the opposite surfaces of the liquid, and consequently its position, will continue unchanged. Hence the differential thermometer stands at the same point, however different may be the temperature of the medium. But the slightest difference between the temperature of the two balls will instantly be detected; for the elasticity of the air on one side being then greater than that on the other, the liquid will retreat towards the ball whose temperature is lowest.

Solid substances are not better suited to the construction of a thermometer than gases; for while the expansion of the latter is too great, that of the former is so small that it cannot be measured except by the adaptation of complicated machinery. Liquids which expand more than the one and less than the other, are exempt from both extremes; and, consequently, we must search among them for a material with which to construct a thermometer. The principle of selection is plain. A material is required whose expansions are uniform, and whose boiling and freezing points are very remote from one another. Mercury fulfils these conditions better than any other liquid. No fluid can support a greater degree of heat without boiling than mercury; and none, except alcohol and ether, can endure a more intense cold without freezing. It has, besides, the additional advantage of being more sensible to the action of heat than other liquids, while its dilatations between 32° and 212° are almost perfectly uniform. Strictly speaking, the same quantity of heat does occasion a greater dilatation at high than at low temperatures, so that, like other fluids, it expands in an increasing ratio. But it is remarkable that this ratio, within the limits assigned, is exactly the same as that of glass; and therefore if contained in a glass tube, the increasing expansion of the vessel compensates for that of the mercury.

We cannot here describe in detail the method of constructing a mercurial thermometer. This well known instrument consists of a tube of a uniform small bore, having a ball blown at one end. The ball and part of the tube are filled with mercury, the air is expelled by boiling the mercury, and the tube is hermetically sealed.

In order to graduate the thermometer, two fixed points are required: these are obtained by immersing it first in melting ice, marking the point at which it stands; and secondly in boiling water, at the level of the sea, and under the usual atmospheric pressure, the point at which it stands being also marked.

The distance between these two points may be divided into any number of equal parts or degress. Fahrenheit, whose scale is commonly used in this country, divided it into 180 degrees, beginning his scale at a point 32 of these degrees below the freezing point of water, which is the zero of his scale. Celsius, the author of the centigrade scale, most frequently employed on the Continent, placed his zero at the freezing point, and divided the distance between that and the boiling point into 100 degrees. Reaumur adopted the same starting point or zero, but divided the same distance into 80 degrees only. Hence, the boiling point of water, on Fahrenheit's scale, is 212°, on the centigrade scale 100°, and on that of Reaumur 80°.

It is easy to reduce the temperature expressed by one thermometer to that of another, by knowing the relation which exists between their degrees. Thus, 180 is to 100 as 9 to 5, and to 80 as 9 to 4; so that nine degrees of Fahrenheit are equal to five of the centigrade, and four of Reaumur's thermometer. Fahrenheit's is therefore reduced to the centigrade scale, by multiplying by five, and dividing by nine; or to that of Reaumur, by multiplying by four instead of five, previously substracting 32°, because the zero of Fahrenheit is 32° lower than that of the others. The same process, reversed, enables us to reduce degrees of the other scales to those of Fahrenheit.

But, to save the trouble of such reductions, I have subjoined a table which shows the degrees on the centigrade scale and that of Reaumur, corresponding to the degrees of Fahrenheit's thermometer.

Fahr.	Cent.	Reaum.	Fahr.	Cent.	Reaum.	Fahr.	Cent.	Reaum.
212	100	80	113	45	36	14	–10	– 8
203	95	76	104	40	32	5	–15	–12
194	90	72	95	35	28	4	–20	–16
185	85	68	86	30	24	–13	–25	–20
176	80	64	77	25	20	–22	–30	–24
167	75	60	68	20	16	–31	–35	–28
158	70	56	59	15	12	–40	–40	–32
149	65	52	50	10	8			
140	60	48	41	5	4			
131	55	44	32	0	0			
122	50	40	23	–5	–4			

The mercurial thermometer may be made to indicate temperatures which exceed 212°, or fall below zero, by continuing the degrees above and below those points. But as mercury freezes at 39 degrees below zero, it cannot indicate temperatures below that point; and indeed the only liquid which has been used for such purposes is alcohol. Our means of estimating high degrees of heat are as yet very unsatisfactory.

The instruments for measuring intense degrees of heat are called *pyrometers*, and must be formed either of solid or gaseous substances. The former alone have been hitherto employed, though the latter, from the greater uniformity with which they expand, are better calculated for the purpose. The action of most pyrometers depends on the elongation of a metallic bar by heat; and the difficulty in their construction consists in finding an infusible metal of uniform expansibility, and in measuring the degree of expansion with exactness. The best of these is Daniell's pyrometer, which, with a little practice, may be used with facility, and appears susceptible of very great precision. (Phil. Trans. 1830 and 31.) It consists of a bar of platinum or soft iron, so placed in a case of black lead earthenware, that when exposed to a high temperature, the bar, expanding more than the case, pushes forward an index of porcelain. The degree to which the index is pushed forward measures the expansion of the bar. Although the expansions of the bar be not strictly uniform at different temperatures, still they afford a good practical index of the relative intensity of different fires, and will be an exact measure of temperature when the precise rate of expansion shall have been determined.

The pyrometer of Wedgewood acts on a different principle, being founded on the property which clay, a compound of aluminous earth and water, possesses of gradually losing its water when exposed to an increasing temperature, and of contracting as the water is dissipated. This instrument, however, is no longer employed by scientific men, because its indications cannot be relied on. Every observation requires a separate piece of clay, and the observer is never sure that the contraction of the second piece, from the same heat, will be exactly similar to that of the first; especially as it is difficult to procure specimens of the earth, the composition of which is in every respect the same.

Though the thermometer is one of the most valuable instruments of philosophical research, it must be confessed that the sum of information which it conveys is very small. It does indeed point out a difference in the temperature of two or more substances with great nicety; but it does not indicate how much heat any body contains. The thermometer gives the same kind of information which may be discovered, though less accurately, by the feelings; it recognizes in bodies that state alone which affects the senses with an impression of heat or cold,—the condition expressed by the word *temperature*. All we learn by this instrument is, whether the temperature of one body is greater or less than that of another; and if there is a difference, it is expressed numerically, namely, by the degrees of the thermometer. But it must be remembered that these degrees are parts of an arbitrary scale, selected for convenience, without any reference whatever to the actual quantity of heat present in bodies.

A little reflection will evince the propriety of these remarks. If two glasses of unequal size be filled with water just taken from the same spring, the thermometer will stand in each at the same height, though their quantities of heat are certainly unequal. This observation naturally suggests the inquiry, whether different kinds of substances, whose temperatures as estimated by the thermometer are the same, contain equal quantities of heat,—if, for example, a pound of iron contains as much heat as a pound of water or mercury. The foregoing remark shows that equality in temperature is not necessarily connected with equality in quantity of heat; and the inference has been amply confirmed by experiment. If equal quantities of water are mixed together, one portion being at 100° and the other at 50°, the temperature of the mixture will be the arithmetical mean or 75°; that is, the 25 degrees lost by the warm water will exactly suffice to heat the cold water by the same number of degrees. It is hence inferred, that equal weights or measures of water of the same temperature contain equal quantities of heat; and the same is found to be true of other bodies. But if equal weights or equal bulks of *different* substances are employed, the result will be different. Thus, if a pint of mercury at 100° be mixed with a pint of water at 40°, the mixture will have a temperature of 60°, so that the 40 degrees lost by the former, heated the latter by 20 degrees only; and when, reversing the experiment, the water is at 100° and the mercury at 40°, the mixture will be at 80°, the 20 degrees lost by the former causing a rise of 40 in the latter. The fact is still more strikingly displayed by substituting equal weights for measures. For instance, on mixing a pound of mercury at 160° with a pound of water at 40°, a thermometer placed in the mixture will stand at 45°: but if the mercury be at 40° and the water at 160°, the mixture will have a temperature of 155°. If water at 100° be mixed with an equal weight of spermaceti oil at 40°, the mixture will be found at 80°; and when the oil is at 100° and the water at 40°, the temperature of the mixture will be only 60°.

It appears from these facts, that the same quantity of heat imparts twice as high a temperature to mercury as to an equal volume of water; that a similar proportion is observed with respect to equal weights of spermaceti oil and water; and that the heat which gives 5 degrees to water will raise an equal weight of mercury by 115 degrees, being the ratio of 1 to 23. Hence if equal quantities of heat be added to equal weights of water, spermaceti oil, and mercury, their temperatures in relation to each other will be expressed by the numbers 1, 2, and 23 ; or, what amounts to the same, in order to increase the temperature of equal weights of those substances to the same extent, the water will require 23 times more heat than the mercury, and twice as much as the oil. The peculiarity exemplfied by these substances, and which it would be easy to illustrate by other examples, was first noticed by Black. It is a law admitted to be universal, and may be thus expressed : that *equal* quantities of different bodies require *unequal* quantities of heat to heat them equally. This difference in bodies was expressed by Black by the term *capacity* for heat, but the term *specific heat* is now generally preferred.

The singular fact of substances of equal temperature containing unequal quantities of heat naturally excites speculation about its cause, and various attempts have been made to account for it. The explanation deduced from the views of Black is the following. He conceived that heat exists in bodies in two opposite states : in one it is supposed to be in chemical combination, exhibiting none of its ordinary characters, and remaining as it were concealed, without evincing any signs of its presence ; in the other, it is free and uncombined, passing readily from one substance to another, affecting the senses in its passage, determining the height of the thermometer, and, in a word, giving rise to all the phenomena which are attributed to this active principle.

Though it would be easy to start objections to this ingenious conjecture, it has the merit of explaining phenomena more satisfactorily than any view that has been proposed in its place. It is entirely consistent with analogy. But in admitting the plausibility of this explanation, it is proper to remember that it is at present entirely hypothetical; and that the language suggested by an hypothesis should not be unnecessarily associated with the phenomena to which it owes its origin. Accordingly, the word *sensible* is better than *free* heat, and *insensible* preferable to *combined* or *latent* heat; for by such terms the fact is equally well expressed, and philosophical propriety strictly preserved.

It is of importance to know the specific heat of bodies. The most convenient method of discovering it, is by mixing different substances together in the way just described, and observing the relative quantities of heat requisite for heating them by the same number of degrees.

This method was first suggested by Black, and was afterwards practised to a great extent by Crawford and Irvine.[*] But the same knowledge may be obtained by reversing the process,—by noting the relative quantities of heat which bodies give out in cooling; for if water require 23 times more heat than mercury to raise its temperature by one or more degrees, it must also lose 23 times as much in cooling. The calorimeter of Levoisier and Laplace is founded on this principle. In this instrument the heat given out by a hot body in cooling is measured by the quantity of ice liquefied by it. But although the principle is unexceptionable, there are difficulties in the application of it which render the calorimeter an incorrect instrument. It is, therefore, unnecessary here to describe it in detail.

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[*] Crawford on Animal Heat, and Irvine's Chemical Essays.

The determination of the sp. heat of gaseous substances is a problem of importance, and has occupied the attention of several experimenters of great science and practical skill; but the inquiry is beset with so many difficulties that, in spite of the talent which has been devoted to it, our best results can be viewed as approximations only, requiring to be corrected by future research. Crawford first investigated this subject, but his results are admitted to have been erroneous, and need not here be cited. Lavoisier and Laplace, by means of the calorimeter, obtained more accurate results; but those most to be depended on were obtained by Delaroche and Bérard by means of a modification of the calorimeter, in which they observed, not how much ice was melted, but how far water was heated by the hot body during its cooling. Their experiments were made with such skill as to inspire great confidence. They are contained in the following table: the sp. heat of the gases being referred to air as unity in the two first columns, and to water in the third.

Names of Substances.	Under equal Volumes and constant Pressure.	Under equal Weights.	
Atmospheric air	1·0000	1·0000	0·2669
Hydrogen gas	0·9033	12·3400	3·2936
Oxygen gas	0·9765	0·8848	0·2361
Nitrogen gas	1·0000	1·0318	0·2754
Nitrous oxide gas	1·3503	0·8878	0·2369
Olefiant gas	1·5530	1·5763	0·4207
Carbonic oxide gas	1·0340	1·0805	0·2884
Carbonic acid gas	1·2583	0·8280	0·2210
Water			1·0000
Aqueous vapour			0·8470

Although objections have been started to these experiments, and other methods of ascertaining the sp. heats of gases proposed by Haycraft, Delarive and Marcet, and others; yet on the whole we may conclude that, although the sp. heats of the gases are not accurately known, the numbers of Delaroche and Bérard are probably the best approximations hitherto published.

The circumstances which merit particular notice, concerning the sp. heats of bodies, may be arranged under the eight following heads :—

1. Every substance has a sp. heat peculiar to itself; whence it follows, that a change of composition will be attended by a change of sp. heat.

2. The sp. heat of a body varies with its form. A solid has a smaller sp. heat than the same substance when in the state of a liquid ; the sp. heat of water, for instance, being 9 in the solid state, and 10 in the liquid. Whether the same weight of a body has a greater sp. heat in the solid or liquid form than in that of vapour, is a circumstance not yet decided.

3. When a given weight of any gas is made to vary in density and volume while its elasticity is unchanged, as when air confined in a tube over mercury is heated and suffered to expand without variation of pressure, the sp. heat is believed to remain constant.

4. Of the sp. heats of equal volumes of the same gas at a varying density and elasticity, as when air is forced into a bottle with different degrees of force, nothing certain has been established.

5. The sp. heats of equal weights of the same gas vary as the density and elasticity vary. Thus, when 100 measures of air expand by diminished pressure to 200 measures, its sp. heat is increased ; and when the same quantity of air is compressed into the space of 50 measures, its sp. heat is diminished. The exact rate of increase is unknown ; but, according to Delaroche and Bérard, the ratio is less rapid than the diminution in density ; that is, the sp. heat of any gas being 1, it is not 2, but between 1 and 2, when its volume is doubled.

6. The sp. heats of solids and liquids were formerly thought, especially by Crawford and Irvine, to be constant at all temperatures, so long as they suffer no change of form or composition, Dalton, however, (Chemical Philosophy, part I. p. 50,) endeavours to show that the sp. heat of such bodies are greater in high than at low temperatures; and Petit and Dulong, in the essay already quoted, have proved it experimentally with respect to several of them.

It is difficult to determine whether the increased sp. heat observed in solids and liquids at high temperatures is owing to the accumulation of heat within them, or to their dilatation. It is ascribed in general to the latter, and I believe correctly; because the expansion and contraction of gases by change of pressure, without the aid of heat, is attended with corresponding changes of sp. heat.

7. Change of sp. heat always occasions a change of temperature. Increase in the former is attended by diminution of the latter; and decrease in the former by increase of the latter. The explanation of these facts is obvious. In the first case, a quantity of heat becomes insensible, which was previously in a sensible state; in the second, heat is evolved, which was previously latent.

8. An important relation between the sp. heats of some elementary substances and their equivalents was discovered by Dulong and Petit, namely, that the product of the sp. heat of each element by the weight of its atom is a constant quantity. This relation, if general, would be of great interest, as leading directly to the inference that the atoms of elementary substances are associated with equal quantities of heat, and enabling chemists to calculate either the sp. heats of elements from their equivalents, or conversely their equivalents from their sp. heats. (An. de Ch. et Ph. x. 403.) The relation above alluded to was exemplified by Dulong and Petit by a table similar to the subjoined.

	Specific Heat.		Relative Weights of Atoms.		Product of the Sp. Heat of each element by the weight of its atom.
Lead	0·0293	×	103·6	=	3·0353
Tin	0·0514	×	57·9	=	2·9760
Zinc	0·0927	×	32·3	=	2·9942
Tellurium	0·0912	×	32·3	=	2·9457
Copper	0·0949	×	31·6	=	2·9988
Nickel	0·1035	×	29·5	=	3·0532
Iron	0·1100	×	28	=	3·0800
Sulphur	0·1880	×	16·1	=	3·0268
Platinum	0·0355	×	98·8	=	3·3098
Bismuth	0·0288	×	71	=	2·0448
Cobalt	0·1498	×	29·5	=	4·4191
Arsenic	0·081	×	37·7	=	3.0537
Carbon	0·25	×	6·12	=	1·5300
Iodine	0·089	×	126·3	=	11·2407
Phosphorus	0·385	×	15·7	=	6·0445
Mercury	0·0330	×	202	=	6·6660
Silver	0·0557	×	108	=	6·0156
Gold	0·0298	×	199·2	=	5·9361

It will be observed, on inspecting the last column of the table, that the product of the sp. heat into the equivalent is very nearly 3 for the first nine substances. Platinum deviates visibly from the law; and bismuth, cobalt, and iodine, strikingly. The four last elements would nearly coincide with the law, were their respective equivalents estimated at half the numbers given in the tables as would carbon were its equivalent doubled. These coincidences are too close and numerous to arise from chance, and justify a belief in the law having a real foundation dependent on the connection between heat and the elementary particles of matter. The researches of Avogadro and Neumann give additional weight to this opinion by tracing the same law in many compound bodies, those compounds alone being compared together whose atomic constitution is similar (An. de Ch. et. Ph. LV. 80, and LVII. 113; and Pog. An. XXIII. 1).

ON LIQUEFACTION.

All bodies are solid, liquid, or gaseous; and the form they assume depends on the relative intensity of cohesion and repulsion. Should the repulsive force be comparatively feeble, the particles will adhere so firmly together, that they cannot move freely upon one another, thus constituting a solid. If cohesion is so far counteracted by repulsion that the particles move on each other freely, a liquid is formed. And should the cohesive attraction be entirely overcome, so that the particles not only move freely on each other, but would, unless restrained by external pressure, separate from one another to an almost indefinite extent, an aëriform substance will be produced.

Now the property of repulsion is manifestly owing to heat; and as it is easy within certain limits to increase or diminish the quantity of this principle in any substance, it follows that the form of bodies may be made to vary at pleasure: that is, by heat sufficiently intense every solid may be converted into a fluid, and every fluid into vapour. This inference is so far justified by experience, that it may safely be considered as a law. The converse ought also to be true; and, accordingly, several of the gases have already been condensed into liquids by means of pressure, and liquids have been solidified by cold. The temperature at which liquefaction takes place is called the melting point, or point of fusion; and that at which liquids solidify, their point of congelation. Both these points are different for different substances, but uniformly the same, under similar circumstances, in the same body.

The most important circumstance relative to liquefaction is Black's discovery that a large quantity of heat disappears, or becomes insensible to the thermometer, during the process. If a pound of water at 32° be mixed with a pound of water at 172°, the temperature of the mixture will be intermediate between them, or 102°. But if a pound of water at 172° be added to a pound of ice at 32°, the ice will quickly dissolve, and on placing a thermometer in the mixture, it will be found to stand not at 102°, but at 32°. In this experiment, the pound of hot water, which was originally at 172°, actually loses 140 degrees of heat, all of which enters into the ice, and causes its liquefaction, but without affecting its temperture; whence it follows that a quantity of heat becomes insensible during the melting of ice, sufficient to raise the temperature of an equal weight of water by 140 degrees. This explains the well known fact on which the graduation of the thermometer depends,—that the temperature of melting ice or snow never exceeds 32°. All the heat which is added becomes insensible, till the liquefaction is complete.

The loss of sensible heat which attends liquefaction seems essentially necessary to the change, and for that reason is frequently called the *heat of fluidity.* The actual quantity of heat required for this purpose varies with the substance, as is proved by the following results obtained by Irvine. The degrees indicate the extent to which an equal weight of each material may be heated by the heat of fluidity which is proper to it.

	Heat of Fluidity.		Heat of Fluidity.
Sulphur	143°68F.	Zinc	493°
Spermaceti	145°	Tin	500°
Lead	162°	Bismuth	550°
Bees-wax	175°		

As so much heat disappears during liquefaction, it follows that heat must be evolved when a liquid passes into a solid. This may easily be proved. The temperature of water in the act of freezing remains at 32°, though exposed to an atmosphere in which the thermometer is at zero. That the water under such circumstances may preserve its temperature, heat must be supplied as fast as it is abstracted: and it is obvious that the only source of supply is the heat of fluidity. Further, if pure recently boiled water be cooled very slowly, and kept very tranquil, its temperature may be lowered to 21°, without any ice being formed; but the least motion causes it to congeal suddenly, and in doing so its temperature rises to 32°. (Blagden in Phil. Trans. 1788.)

The explanation which Black gave of these phenomena constitutes what is called his *doctrine* of *latent heat*, which was partially explained on a former occasion. He conceived that heat in causing fluidity loses its property of acting on the thermometer in consequence of combining chemically with the solid substance, and that liquefaction results, because the compound so formed does not possess that degree of cohesive attraction on which solidity depends. When a liquid is cooled to a certain point, it parts with its heat of fluidity, which is set free or becomes sensible, and the cohesion natural to the solid is restored. The same mode of reasoning was applied by Black to the conversion of liquids into vapours, a change during which a large quantity of heat disappears.

A different explanation of the phenomena was proposed by Irvine. Observing that a solid has a smaller sp. heat than the same substance while liquid, he argued that this circumstance alone accounts for heat becoming insensible during liquefaction. For since the sp. heat of ice and water, or in other words, the quantity of heat required to raise their temperature by the same number of degrees, was found to be as 9 to 10, Irvine inferred that ice must contain one-tenth less heat than water of the same temperature, and that as this difference must be supplied to the ice when it is converted into water, the change must necessarily be accompanied with the disappearance of heat. Irvine applied the same argument to the liquefaction of all solids, and likewise to account for the heat which is rendered insensible during the formation of vapour.

Two objections may properly be urged against the opinion of Irvine. In the first place, no adequate reason is assigned for the liquefaction. It accounts for the disappearance of heat which accompanies liquefaction, but does not explain why the body becomes liquid; whereas the hypothesis of Black affords an explanation both of the change itself, and of the phenomena that attend it. But the second objection is still more conclusive. Irvine argued on the belief that a liquid has in every case a greater sp. heat than when solid: and though this point has not been demonstrated in a manner entirely decisive, yet from the experiments hitherto made, it appears that liquids in general have greater sp. heats than solids, and that therefore Irvine's assumption is probably correct in regard to them. In like manner he believed vapours to have greater sp. heats than the liquids that yield them; but from the fact of most gases having smaller sp. heats than liquids, it is probable that the sp. heats of elastic fluids in general are inferior to those of the liquids from which they are derived. The disappearance of heat during vaporization is not explicable on the views of Irvine; it is necessary to employ the theory of Black to account for that change, and therefore the same doctrine should be applied to the analogous phenomenon of liquefaction.

The loss of sensible heat in liquefaction is the basis of many artificial processes for producing cold, all of which are founded on the principle of liquefying solid substances without supplying heat. The heat of fluidity being then derived from that which had previously existed within the solid itself in a sensible state, the temperature necessarily falls. The degree of cold thus produced depends upon the quantity of heat which disappears; and this again is dependent on the quantity of solid matter liquefied, and on the rapidity of liquefaction.

The most common method of producing cold is by mixing together equal parts of snow and salt. The salt causes the snow to melt by reason of its affinity for water, and the water dissolves the salt; so that both of them become liquid. The cold thus generated is 32 degrees below the temperature of freezing water; that is, a thermometer placed in the mixture would stand at zero. This is the way originally proposed by Fahrenheit for determining the commencement of his scale.

Any other substances which have a strong affinity for water may be substituted for the salt; and those have the greatest effect in producing cold whose affinity for that liquid is greatest, and which consequently produce the most rapid liquefaction. Crystallized chloride of calcium, proposed by Löwitz, is by far the most convenient in practice. It may be made by dissolving marble in hydrochloric acid, and concentrating the solution by evaporation, till, upon letting a drop of it fall upon a cold saucer, it becomes a solid mass. It should then be withdrawn from the fire, and when cold be speedily reduced to a fine powder. From its extreme deliquescence it must be preserved in well-stopped vessels. The following table by Mr. Walker contains the best proportions for producing intense cold. (Phil. Trans. 1801.)

FRIGORIFIC MIXTURES WITH SNOW.*

MIXTURES.	Parts by Weight.	Thermometer sinks.		Degree of Cold produced.
Sea-salt Snow	1 2	From any Temperature	to —5°	
Sea-salt Hydrochlorate of Ammonia Snow	2 1 5		to —12°	
Sea-salt Hydrochlorate of Ammonia Nitrate of Potassa Snow	10 5 5 24		to —18°	
Sea-salt Nitrate of Ammonia Snow	5 5 12		to —25°	

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* The snow should be freshly fallen, dry, and uncompressed. If snow cannot be had, finely pounded ice may be substituted for it.

MIXTURES.	Parts by Weight.	Thermometer sinks.	Degree of Cold produced.
Diluted Sulphuric Acid* Snow	2 3	from +32° to —23°	55 degrees.
Concentrated Hydrochloric Acid Snow	5 8	from +32° to —27°	59
Concentrated Nitrous Acid Snow	4 7	from +32° to —30°	62
Chloride of Calcium Snow	5 4	from +32° to —40°	72
Crystallized Chloride of Calcium Snow	3 2	from +32° to —50°	82
Fused Potassa Snow	4 3	from +32° to —51°	83

Freezing mixtures are also made by the rapid solution of salts, without the use of snow or ice; the following table, by Walker, includes the most important of them. The salts must be finely powdered and dry. (Phil. Trans. 1795.)

MIXTURES.	Parts by Weight.	Temperature falls.	Degree of Cold produced.
Hydrochlorate of Ammonia Nitrate of Potassa Water	5 5 16	from +50° to +10°	40 degrees.
Hydrochlorate of Ammonia Nitrate of Potassa Sulphate of Soda Water	5 5 8 16	from +50° to +4°	46
Nitrate of Ammonia Water	1 1	from +50° to +4°	46
Nitrate of Ammonia Carbonate of Soda Water	1 1 1	from +50° to —7°	57
Sulphate of Soda Diluted Nitrous Acid†	3 2	from +50° to —3°	53
Sulphate of Soda Hydrochlorate of Ammonia Nitrate of Potassa Diluted Nitrous Acid	6 4 2 4	from +50° to —10°	60
Sulphate of Soda Nitrate of Ammonia Diluted Nitrous Acid	6 5 4	from +50° to —14°	64
Phosphate of Soda Diluted Nitrous Acid	9 4	from +50° to —12°	62
Phosphate of Soda Nitrate of Ammonia Diluted Nitrous Acid	9 6 4	from +50° to —21°	71
Sulphate of Soda Hydrochloric Acid	8 5	from +50° to 0°	50
Sulphate of Soda Diluted Sulphuric Acid‡	5 4	from +50° to +3°	47

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* Made of strong acid, diluted with half its weight of snow or distilled water.

† Composed of fuming nitrous acid 2 parts in weight, and one of water; the mixture being allowed to cool before being used.

‡ Composed of equal weights of strong acid and water, being allowed to cool before use.

These artificial processes for generating cold are much more effectual when the materials are previously cooled by immersion in other frigorific mixtures. One would at first suppose that an unlimited degree of cold might be thus produced; but it is found that when the difference between the mixture and the air becomes very great, the communication of heat from one to the other becomes so rapid, as to put a limit to the reduction. The greatest cold produced by Walker did not exceed 100 degrees below the zero of Fahrenheit.

Though we shall probably never succeed in depriving any substance of all its heat, bodies doubtless contain a certain definite quantity of this principle, and various attempts have been made to calculate its amount.

To be satisfied that such calculations cannot be trusted, it is sufficient to know that the estimates made by different chemists respecting the absolute quantity of heat in water vary from 900 to nearly 8000.*

VAPORIZATION.

Aëriform substances are commonly divided into vapours and gases. The former are characterised by their ready conversion into liquids or solids, either by a moderate increase of pressure, the temperature at which they were formed remaining the same, or by a moderate diminution of that temperature, without change of pressure. Gases, on the contrary, retain their elastic state more obstinately: they are always gaseous at common temperatures; and, with one or two exceptions, cannot be made to change their form, unless by being subjected to much greater pressure than they are naturally exposed to. Several of them, indeed, have hitherto resisted every effort to compress them into liquids. The only difference between gases and vapours is in the relative forces with which they resist condensation.

Heat is the cause of vaporization as well as of liquefaction. A sufficiently intense heat would doubtless convert every liquid and solid into vapour. Some bodies, however, resist the strongest heat of our furnaces without vaporizing. These are said to be *fixed* in the fire; those which, under the same circumstances, are converted into vapour, are called *volatile*.

The disposition of various substances to yield vapour is very different; and the difference depends doubtless on the relative power of cohesion with which they are endowed. Fluids, in general, are more easily vaporized than solids, as would be expected from the weaker cohesion of the former. Some solids, such as arsenic and sal-ammoniac, pass at once into vapour without being liquefied; but most of them become liquid before assuming the elastic condition.

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* Dalton's New System of Chemical Philosophy.

Vapours occupy more space than the substances from which they were produced. Gay-Lussac found that water, in passing from its point of greatest density into vapour, expands to 1696 times its volume, alcohol to 659 times, and ether to 443 times, each vapour being at 212° and under a pressure of 29·92 inches of mercury. This shows that vapours differ in density. Watery vapour is lighter than air at the same temperature and pressure in the ratio of 1000 to 1604; or the sp. gr. of air being 1000, that of watery vapour is 625. The vapour of alcohol, on the contrary, is half as heavy again as air; and that of ether is more than twice and a half as heavy.

The dilatation of vapours by heat was found by Gay-Lussac to follow the same law as gases; that is, for every degree of Fahrenheit, they increase by $\frac{1}{480}$th of the volume they occupied at 32°. But this law only holds of vapours when separated from the liquids that yield them. If liquid be present heat not only expands the vapour but increases its volume by the addition of a new quantity of vapour. In like manner, the contraction of a vapour by cold will deviate from the above law, as soon as the cold condenses any part of it into liquid.

Vapours vary in volume under varying pressure according to the same law as gases, provided always that the gaseous state is preserved. This law, which was discovered by Boyle and Mariotte, and is more fully explained in the section on atmospheric air, merely expresses the fact that the volume of gaseous substances at a constant temperature is inversely as the pressure to which they are subject.

Vaporization is conveniently studied under two heads,—*Ebullition* and *Evaporation*. In the first, the production of vapour is so rapid that its escape gives rise to a visible commotion in the liquid; in the second, it passes off quietly and insensibly.

EBULLITION.

The temperature at which vapour rises with sufficient freedom for causing the phenomena of ebullition, is called the *boiling point*. The heat requisite for this effect varies with the nature of the fluid. Thus, sulphuric ether boils at 96°, alcohol at 176°, and pure water at 212°; while oil of turpentine must be raised to 316°, and mercury to 662°, before either exhibits marks of ebullition. The boiling point of the same liquid is constant, so long as the necessary conditions are preserved; but it is liable to be affected by several circumstances. The nature of the vessel has some influence upon it. Thus Gay-Lussac observed that pure water boils precisely at 212° in a metallic vessel, and at 214° in one of glass, owing apparently to its adhering to glass more powerfully than to a metal. It is likewise affected by the presence of foreign particles: when a few iron filings are thrown into water boiling in a glass vessel, its temperature quickly falls from 214° to 212°, and remains stationary at the latter point. But the circumstance which has the greatest influence over the boiling point of liquids is variation of pressure. All bodies upon the earth are constantly exposed to considerable pressure; for the atmosphere itself presses with a force equivalent to a weight of 15 pounds on every square inch of surface. Liquids are exposed to this pressure as well as solids, and their tendency to take the form of vapour is very much counteracted by it. In fact, they cannot enter into ebullition at all, till their particles have acquired such elastic force as enables them to overcome the pressure upon their surfaces; that is, till they press against the atmosphere with the same force as the atmosphere against them. Now the atmospheric pressure is variable, and hence it follows that the boiling point of liquids must also vary.

The pressure of the atmosphere is equal to a weight of 15 pounds on every square inch of surface, when the barometer stands at 30 inches, and then only does water boil at 212°. If the pressure be less, that is, if the barometer fall below 30 inches, then the boiling point of water and every other liquid will be lower than usual; or if the barometer rise above 30 inches, the temperature of ebullition will be proportionally increased. On this account water boils at a lower temperature on the top of a hill than in the valley beneath it; for as the column of air diminishes in length as we ascend, its pressure must likewise suffer a proportional diminution. The ratio between the depression of the boiling point and the diminution of the atmospheric pressure is so exact, that it has been proposed as a method for determining the heights of mountains. An elevation of 530 feet makes a diminution of one degree. (Wollaston in Phil. Trans. for 1817.)

The influence of the atmosphere over the point of ebullition is best shown by removing its pressure altogether. Robison found that fluids boil *in vacuo* at a temperature 140° lower than in the open air. (Black's Lectures, I. 151.)

Water cannot be heated under common circumstances beyond 212°, because it then acquires such expansive force as enables it to overcome the atmospheric pressure, and fly off in the form of vapour. But if subjected to sufficient pressure, it may be heated to any extent without boiling. This is best done by heating water while confined in a strong copper vessel, called Papin's Digester. In this apparatus, on the application of heat, a large quantity of vapour collects above the water, and checks ebullition by the pressure which it exerts upon the surface of the liquid. There is no limit to the degree to which water may thus be heated, provided the vessel is strong enough to confine the vapour ; but the expansive force of steam under these circumstances is so enormous as to overcome the greatest resistance.

Robison (Brewster's edition of his works, p. 25) found that the tension of steam is equal to two atmospheres at 244°, and to three at 270°. The results of Southern's experiments, given in the same volume, fix upon 250·3^0 as the temperature of which steam has the force of two atmospheres, on 293·4^0 for four, and 343·6^0 for eight atmospheres.

This subject has been examined by a commission appointed by the Parisian Academy of Sciences, and Dulong and Arago took a leading part in the inquiry. The results, which are given in the following table, were obtained by experiment up to a pressure of 25 atmospheres, and at higher pressures by calculation. (Brande's Journal, N.S. viii. 191.)

Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.	Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.
1	212	13	380·66
1½	233·96	14	386·94
2	250·52	15	392·86
2½	263·84	16	398·48
3	275·18	17	403·82
3½	285·08	18	408·92
4	293·72	19	413·78
4½	300·28	20	418·46
5	307·5	21	422·96
5½	314·24	22	427·28
6	320·36	23	431·42
6½	326·26	24	435·56
7	331·70	25	439·34
7½	336·86	30	457·16
8	341·78	35	472·73
9	350·78	40	486·59
10	358·88	45	491·14
11	366·85	50	510·60
12	374·00		

The elasticity of steam is employed as a moving power in the steam-engine. The construction of this machine depends on two properties of steam, namely, the expansive force communicated to it by heat, and its ready conversion into water by cold.

The formation of vapour is attended, like liquefaction, with loss of sensible heat. This is proved by the well-known fact that the temperature of steam is precisely the same as that of the boiling water from which it rises; so that all the heat which enters into the liquid is solely employed in converting a portion of it into vapour, without affecting the temperature of either, provided the latter is permitted to escape with freedom. The heat, which then becomes latent, to use the language of Black, is again set free when the vapour is condensed into water. The exact quantity of heat rendered insensible by vaporization may therefore be ascertained by condensing the vapour in cold water, and observing the rise of temperature which ensues. From the experiments of Black and Watt, conducted on this principle, steam of 212°, in being condensed into water of 212°, gives out as much heat as would raise the temperature of an equal weight of water by 950 degrees, all of which had previously existed in the vapour without being sensible to a thermometer.

The latent heat of steam and several other vapours has been examined by Dr. Ure, whose results are contained in the following table. (Phil. Trans. for 1818.)

	Latent heat.
Vapour of Water at its boiling point . .	967°
Alcohol	442
Ether	302·379
Petroleum . . .	177·87
Oil of Turpentine . . .	177·87
Nitric acid . . .	531·99
Liquid ammonia . . .	837·28
Vinegar	875

The disappearance of heat that accompanies vaporization was explained by Black and Irvine, in the way already mentioned under the head of liquefaction; and as the objections to the views of Irvine were then stated, it is unnecessary to mention them on the present occasion.

The variation of volume and elasticity in vapours is attended, as in gases, with a change of sp. heat and a consequent variation of temperature. Thus when steam, highly heated and compressed in a strong boiler, is permitted to escape by a large aperture, the sudden expansion is attended with a great loss of sensible heat: its temperature instantly sinks so much, that the hand may be held in the current of vapour without inconvenience. The same principle accounts for the fact, first ascertained by Watt, that distillation at a low temperature is not attended with any saving of fuel. For when water boils at a low temperature in a vacuum, the vapour is in a highly expanded state, and contains more insensible heat than steam of greater density.

EVAPORATION.

Evaporation as well as ebullition consists in the formation of vapour, and the only assignable difference between them is, that the one takes place quietly, the other with the appearance of boiling. Evaporation occurs at common temperatures. This fact may be proved by exposing water in a shallow vessel to the air for a few days, when it will gradually diminish, and at last disappear entirely. Most fluids, if not all of them, are susceptible of this gradual dissipation ; and it may also be observed in some solids, as for example in camphor. Evaporation is much more rapid in some fluids than in others, and it is always found that those liquids the boiling point of which is lowest evaporate with the greatest rapidity. Thus alcohol, which boils at a lower temperature than water, evaporates also more freely ; and ether, whose point of ebullition is yet lower than that of alcohol, evaporates with still greater rapidity.

The chief circumstances that influence the process of evaporation are extent of surface, and the state of the air as to temperature, dryness, stillness, and density.

1. Extent of surface. Evaporation proceeds only from the surface of fluids, and therefore, *cæteris paribus*, must depend upon the extent of surface exposed.

2. Temperature. The effect of heat in promoting evaporation may easily be shown by putting an equal quantity of water into two saucers, one of which is placed in a warm, the other in a cold situation. The former will be quite dry before the latter has suffered appreciable diminution.

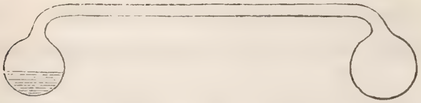
3. State of the air as to dryness or moisture. When water is covered by a stratum of dry air, the evaporation is rapid even when its temperature is low. Thus in dry cold days in winter, the evaporation is exceedingly rapid ; whereas it goes on very tardily if the atmosphere contain much vapour, even though the air be very warm.

4. Evaporation is far slower in still air than in a current, and for an obvious reason. The air immediately in contact with the water soon becomes moist, and thus a check is put to evaporation. But if the air be removed from the surface of the water as soon as it has become charged with vapour, and its place supplied with fresh dry air, then the evaporation continues without interruption.

5. Pressure on the surface of liquids has a remarkable influence over evaporation. This is easily proved by placing ether in the vacuum of an air pump, when vapour rises so abundantly as to produce ebullition.

As a large quantity of heat passes from a sensible to an insensible state during the formation of vapour, it follows that cold should be generated by evaporation. The fact may readily be proved by letting a few drops of ether evaporate from the hand, when a strong sensation of cold will be excited; or if the bulb of a thermometer, covered with lint, be moistened with ether, the production of cold will be marked by the descent of the mercury. But to appreciate the degree of cold which may be produced by evaporation, it is necessary to render it very rapid and abundant by artificial processes; and the best means of doing so is by removing pressure from the surface of volatile liquids. Water placed under the exhausted receiver of an air-pump evaporates with great rapidity, and so much cold is generated as would freeze the water, did the vapour continue to rise for some time with the same velocity. But the vapour itself soon fills the vacuum, and retards the evaporation by pressing upon the surface of the water. This difficulty may be avoided by putting under the receiver a substance, such as sulphuric acid, which has the property of absorbing watery vapour, and consequently of removing it as quickly as it is formed. Such is the principle of Leslie's method for freezing water by its own evaporation.*

The action of the cryophorus, an ingenious contrivance of the late Dr. Wollaston, depends on the same principle. It consists of two glass balls, perfectly free from air, and joined together by a tube as here represented.—One of the balls contains a portion of distilled water, while the other parts of the instrument, which appear empty are full of aqueous vapour, which checks the evaporation from the water by the pressure it exerts upon its surface. But when the empty ball is plunged into a freezing mixture, all the vapour within it is condensed; evaporation commences from the surface of the water in the other ball, and it is frozen in two or three minutes by the cold thus produced.



Liquids which evaporate more rapidly than water, cause a still greater reduction of temperature. The cold produced by the evaporation of ether in the vacuum of the air-pump is so intense as, under favourable circumstances, to freeze mercury.†

The most intense cold yet known is produced by the evaporation in vacuo of condensed gases, such as carbonic acid and sulphurous acid. The carbonic acid, being solid, is dissolved in ether when the object is to produce a very intense cold. (See Carbonic Acid.)

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* See art. Cold, in the Supplement to the Encyclopædia Britannica.

† See a paper by the late Dr. Marcet, in Nicholson's Journal, vol. xxxiv.

Scientific men have differed concerning the cause of evaporation. It was once supposed to be owing to chemical attraction between the air and water, and the idea is at first view plausible, since a certain degree of affinity does to all appearance exist between them. But it is nevertheless impossible to attribute the effect to this cause. For evaporation takes place equally *in vacuo* as in the air; nay, it is an established fact, that the atmosphere positively retards the process, and that one of the best means of accelerating it is by removing the air altogether. The experiments of Dalton prove that heat is the true and only cause of the formation of vapour. He finds that the actual quantity of vapour which can exist in any given space is dependent solely upon the temperature.

Dalton also found that the tension or elasticity of vapour is always the same, however much the presure may vary, so long as the temperature remains constant, and there is liquid enough present to preserve the state of saturation proper to the temperature. This law holds good, whether the vapour be pure, or mixed with air or any other gas.

The elasticity of watery vapour at temperatures below 212° was carefully examined by Dalton (Manchester Memoirs, vol. v.); and his results, together with those since published by Ure (Phil. Trans. 1818), are presented in a tabular form at the end of the volume. They were obtained by introducing a portion of water into the vacuum of a common barometer, and estimating the tension of its vapour by the extent to which it depressed the column of mercury at different temperatures.

A knowledge of the influence of heat and pressure over the volume of gaseous matter is elegantly employed in calculating the sp. gr. of vapour; but before giving the mode of making the calculation, it will be useful to explain what is meant by *specific gravity* or *density*. These terms are generally used to denote the compactness of a substance, or the quantity of ponderable matter contained in a body compared with the space which it occupies. The sp. gr. of a substance is found by dividing its weight by its volume. Thus, if d, w, v, represent the sp. gr. weight and volume of aqueous vapour, and d', w', v', the sp. gr. weight and volume of air, then $d = \frac{w}{v}$, and $d' = \frac{w'}{v'}$. Hence, comparing these sp. gravities, $d : d' :: \frac{w}{v} : \frac{w'}{v'}$; if the volumes are equal, then $d : d' :: w : w'$; and if the weights are equal, $d : d' :: \frac{1}{v} : \frac{1}{v'}$. Consequently the sp. gravities of substances which have an equal volume are directly as their weights; and when the weights are equal, the sp. gravities are inversely as the volumes. Accordingly, if we weigh an equal volume of any number of substances, temperature and pressure being the same in all, the sp. gr. of each respectively will be represented by its weight. Thus, Gay-Lussac ascertained that if a certain volume of air at 212° and 30 Bar. weigh 1000 grains, an equal volume of aqueous vapour, at the same temperature and pressure, will weigh 625 grains; and, therefore, the sp. gr. of steam is 625 compared to that of air as 1000. Atmospheric air is universally taken as a term of comparison for the sp. gr. of gaseous substances, and pure water for that of liquids and solids.

It admits of inquiry whether liquids of weak volatility, such as mercury and oil of vitriol, give off any vapour at common temperatures. An opinion has prevailed, that evaporation not only takes place from the surface of these and similar liquids at all times, but that vapour of exceedingly weak tension is emitted at common temperatures from all substances however fixed in the fire, even from the earths and metals, when they are either in a vacuum or surrounded by gaseous matter. It has accordingly been supposed, that the atmosphere contains diffused through it minute quantities of the vapours of all the bodies with which it is in contact; and this idea has been made the basis of a theory of the origin of meteorites. But this doctrine has been successfully combated by Faraday, in his essay On the Existence of a Limit to Vaporization (Phil. Trans. 1826). He has there shown that in many substances the forces of gravity and cohesion are sufficient to overpower elasticity, and that at ordinary temperatures they give off no vapour whatever.

The presence of vapour has a considerable influence over the bulk of gases; and as chemists often determine the quantity of gaseous substances by measure, it is important to estimate the increase of volume due to the presence of moisture. The mode by which a vapour acts is obvious. When two gases which do not act chemically on each other, are intermingled, each retains the elasticity suited to its volume, exactly as if the other gas were absent: so that the elasticity of the mixture is the sum of the elastic forces of its ingredients. The same remark applies to the mixture of gases and vapours. If a few drops of water are added to a portion of dry air, confined in a glass tube over mercury, the air will speedily become saturated with vapour, and must in consequence be increased in bulk. For the elastic power of the vapour being added to that previously exerted by the gas alone, the mixture will necessarily exert a stronger pressure upon the mercury that confines it, and will therefore occupy a greater space. It is equally clear that the degree of augmentation will depend on the temperature: for it is the temperature alone which determines the elasticity of the vapour.

As the elasticity of vapour is not at all affected by mere admixture with gases, it is easy to correct the fallacy to which its presence gives rise, by means of the data furnished by the experiments of Dalton. The formula for the correction is thus deduced. Let n be the bulk of dry air or other gas expressed in the degrees of a graduated tube; p the elasticity of the dry air, equal to the atmospheric pressure as measured by a barometer; n' the bulk of the air when saturated with watery vapour, and f the elasticity of that vapour (Biot's Traité de Phys. I. 303). Now, as the elasticity of a gas for equal temperatures is inversely as its volume, it follows that when the dry air increases in bulk from n to n', its elasticity will diminish in the ratio of n' to n. Hence its elasticity ceases to be $= p$, and is expressed by $\frac{pn}{n'}$; p is then $= \frac{pn}{n'} + f$; that is, the elasticity of the moist air, added to the elasticity of the vapour present, is equal to the pressure of the atmosphere. From this last equation are deduced the following values: $pn + fn' = pn'$; $pn = pn' - fn'$; and $n = \frac{n'(p-f)}{p}$. One example will suffice for showing the use of this formula. Having 100 measures of air saturated with watery vapour at 60°, the barometer standing at 30 inches, how many measures would the air occupy if quite dry? $n' = 100$; $p = 30$; $f = 0{\cdot}524$, the tension of watery vapour at 60°, according to Dalton's table.* Hence $n = \frac{100 \times (30 - 0{\cdot}524)}{30} = \frac{100 \times 29{\cdot}476}{30} = 98{\cdot}25$, which is the answer required.

The quantity of vapour present in the atmosphere is very variable, in consequence of the continual change of temperature to which the air is subject. But even when the temperature is the same, the quantity of vapour is still found to vary; for the air is not always in a state of saturation. At one time it is excessively dry, at another it is fully saturated; and at other times it varies between these extremes. This variable condition of the atmosphere as to saturation is ascertained by the hygrometer.

A great many hygrometers have been invented; but they may all be referred to three principles. The construction of the first kind of hygrometer is founded on the property possessed by some substances of expanding in a humid atmosphere, owing to a deposition of moisture within them; and of parting with it again to a dry air, and in consequence contracting. Of these, none is better than the human hair, which not only elongates freely from imbibing moisture, but by reason of its elasticity, recovers its original length on drying. The hygrometer of Saussure is made with this material.

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* Manchester Memoirs, vol. v.

The second kind of hygrometer points out the opposite states of dryness and moisture by the rapidity of evaporation. Water does not evaporate at all when the atmosphere is completely saturated with moisture; and the freedom with which it goes on at other times is in proportion to the dryness of the air. The hygrometric condition of the air may be determined, therefore, by observing the rapidity of evaporation. The most convenient method of doing this is by covering the bulb of a thermometer with a piece of silk or linen, moistening it with water, and exposing it to the air. The descent of the mercury, or the cold produced, will correspond to the quantity of vapour formed in a given time. Leslie's hygrometer is of this kind.

The third kind of hygrometer is on a principle entirely different from the foregoing. When the air is saturated with vapour, and any colder body is brought into contact with it, deposition of moisture immediately takes place on its surface. The degree indicated by the thermometer when dew begins to be deposited, is called the *dew-point.* If the saturation be complete, the least diminution of temperature is attended with the formation of dew; but if the air is dry, a body must be several degrees colder before moisture is deposited on its surface; and indeed the drier the atmosphere, the greater will be the difference between its temperature and the dew-point. Attempts were made to estimate the hygrometric state of the air on this principle by the Florentine Academicians, but the first accurate method was introduced by Le Roi, and since adopted by Dalton. It consists simply in putting cold water into a glass vessel, the outside of which is carefully dried, and marking the temperature of the liquid at which dew begins to be deposited on the glass. The water when necessary is cooled either by means of ice or a freezing mixture. A convenient form of apparatus is a small cup made of thin silver, nicely gilt on the outside, capable of holding about half an ounce of water, and fitted into a case of turned wood lined with cloth, which serves as a stand for the cup during an observation. The water is cooled by successively adding a few grains of a powder made of equal parts of nitre and sal-ammoniac intimately mixed, stirring with the bulb of a small thermometer. As soon as dew is deposited, the temperature is noted ; and the first observation is corrected by waiting until the cup and its contents grow warmer, and observing the temperature at which the dew begins to disappear. The last observation is the most trustworthy. This method, when deliberately performed, so that the cup, the solution, and the thermometer should have time to acquire the same temperature, is susceptible of great precision.

The hygrometer of Daniell, described in his Meteorological Essays, acts on the same principle. It consists of a cryophorus, as described at page 46, but modified somewhat in form, and containing ether instead of water. Within one of its balls is fixed a delicate thermometer, the bulb of which is partially immersed in the ether so as to indicate its temperature, and the other ball is covered with muslin. When the instrument is used the muslin is moistened with ether, and the cold produced by its evaporation condenses the vapour within the cryophorus, and causes the ether to evaporate rapidly in the other ball. The cold thus generated chills the ether itself and the ball containing it ; and in a short time its temperature descends so low, that dew is deposited on the surface of the glass. As soon as this takes place, the temperature is observed by the thermometer.

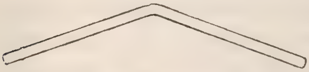
The same object is attained in a still easier way by means of a contrivance described by Jones of London (Phil. Trans. 1826), and soon after by Coldstream of Leith (Phil. Journ. ix. 155). It consists of a delicate mercurial thermometer, the bulb of which is made of thin black glass, and, excepting about a fourth of its surface, is covered with muslin. On moistening the muslin with ether, the temperature of the bulb and mercury falls, and the uncovered portion of the bulb is soon rendered dim by the deposition of moisture. The temperature indicated at that instant by the thermometer is the dew-point.

It is desirable on some occasions, not merely to know the hygrometric condition of air or gases, but also to deprive them entirely of their vapour. This may be done to a great extent by exposing them to intense cold ; but the method now generally preferred is by bringing the moist gas in contact with some substance which has a powerful chemical attraction for water. Of these none is preferable to chloride of calcium, except in the case of ammoniacal gas.

CONSTITUTION OF GASES WITH RESPECT TO HEAT.

From the experiments of Faraday on the liquefaction of gaseous substances, gases may be viewed as the vapours of extremely volatile liquids. Most of these liquids, however, are so volatile, that their boiling point, under the atmospheric pressure, is lower than any natural temperature; and hence they are always found in the gaseous state. By subjecting them to great pressure, aided in the case of many of them, by intense cold, their elasticity is so far counteracted that they become liquid. But even when thus compressed, a very moderate heat is sufficient to make them boil; and on the removal of pressure they resume the elastic form, most of them with such violence as to cause a report like an explosion, and others with the appearance of brisk ebullition. Intense cold is produced at the same time, in consequence of their heat passing from a sensible to an insensible state.

The process for condensing certain gases (Philos. Trans. 1823) consists in exposing them to the pressure of their own atmospheres. The materials for producing the gas are put into a strong glass tube, which is afterwards sealed hermetically, and bent in the middle, as represented by the figure. The gas is generated, if necessary, by the application of heat; and when the pressure becomes sufficienly great, the liquid is formed and collects in the free end of the tube, which is kept cool to facilitate the condensation. Most of these experiments are attended with danger from the bursting of the tubes, against which the operator must protect himself by the use of a mask.



The pressure required to liquefy gases is very variable, as will appear from the following table of the results obtained by Faraday.

Sulphurous acid gas	2	atmospheres at	45°
Sulphuretted hydrogen gas	17		50°
Carbonic acid gas	36		32°
Chlorine gas	4		60°
Nitrous oxide gas	50		45°
Cyanogen gas	3·6		45°
Ammoniacal gas	6·5		50°
Muriatic acid gas	40		50°

Additional light has been thrown on the nature of gases by M. Thilorier, who has succeeded in obtaining carbonic acid in a solid state (Ann. de Ch. et. Ph. lx. 431). It is procured by directing a jet of the liquid carbonic acid into a small glass phial, which is rapidly filled with solid carbonic acid in the form of a white flocculent powder. The solidification is evidently produced by the cold occasioned by the sudden transition of a liquid into a gas, in which state it occupies a space 400 times greater than its original volume. The degree of cold thus produced is estimated by Thilorier at—148°, at which temperature carbonic acid appears to be entirely deprived of its elastic force; for the solid exposed to the ordinary atmospheric pressure and temperature evaporates slowly and quietly, and is gradually converted into carbonic acid gas.

Faraday has, recently, by employing solid carbonic acid, mixed with ether, to produce intense cold by its evaporation in vacuo, and exposing a number of gases to this cold and to high pressure at the same time, succeeded in liquefying not only the gases in the above list, but also olefiant gas, hydriodic acid, hydrobromic acid, fluosilicic acid, phosphuretted hydrogen, fluoboric acid, peroxide of chlorine, and arseniuretted hydrogen gases.

Of the gases thus liquefied, the following were also solidified by Faraday, by means of the intense cold above-mentioned; namely, hydriodic acid, hydrobromic acid, sulphurous acid, sulphuretted hydrogen, peroxide of chlorine, protoxide of nitrogen (nitrous oxide), cyanogen, and ammonia.

It is probable that by means of solidified nitrous oxide, used in the same same way as carbonic acid, cold may be produced sufficiently intense to liquefy those gases which have hitherto resisted our efforts.

The following gases have not yet been liquefied, although exposed to a cold of from 120° to 170° below the freezing point of water, and to pressures varying from 27 to 50 atmospheres; namely, hydrogen, oxygen, nitrogen, nitric oxide, carbonic oxide, coal gas. Oxygen has resisted a temperature of 145°, combined with a pressure of 58·5 atmospheres.

Further details of these interesting results will be found under the different gases.

SOURCES OF HEAT.

The sources of heat may be reduced to six:—1. The sun. 2. Combustion. 3. Electricity. 4. The bodies of animals during life. 5. Chemical action. 6. Mechanical action.—All these means of procuring a supply of heat, except the last, will be more conveniently considered in other parts of the work.

The mechanical method of exciting heat is by friction and percussion. When parts of heavy machinery rub against one another, the heat excited, if the parts of contact are not well greased, is sufficient for kindling wood. The axle-trees of carriages have been burned from this cause, and the sides of ships are said to have taken fire by the rapid descent of the cable. Count Rumford has given an interesting account of the heat excited in boring cannon, which was so abundant as to heat a considerable quantity of water to its boiling point. It appeared from his experiments that a body never ceases to give out heat by friction, however long the operation may be continued; and he inferred from this observation that heat cannot be a material substance, but is merely a property of matter. Pictet observed that solids alone produce heat by friction, no elevation of temperature taking place from the mere agitation of fluids with one another. He found that the heat excited by friction is not in proportion to the hardness and elasticity of the bodies employed. On the contrary, a piece of brass rubbed with a piece of cedar wood produced more heat than when rubbed with another piece of metal; and the heat was still greater when two pieces of wood were employed.

SECTION II.

LIGHT.

Optics, from *οπτομαι I see*, is the science which treats of light and vision. On the nature of light two rival theories exist, the *undulatory* and *corpuscular*. Prior to and about the time of Newton's celebrated analysis of solar light in 1672, Descartes, Hooke, Huygens, and others, had entertained the former; but Newton, in adopting the latter, led to its almost general reception. He considered light to consist of inconceivably minute particles, too subtile to exhibit the common properties of matter, though really material, which emanate from luminous bodies, such as the sun, the fixed stars, and incandescent substances, travel with immense velocity, and excite the sensation of light by passing bodily through the substance of the eye, and striking against the expanded nerve of vision, the retina. This theory, with which the language of optics has become identified, prevailed with almost no opposition from the time of Newton till 1801, when the undulation theory was revived and supported with great ability by Young (Phil. Trans.). By the researches of others, the testimony in favour of this doctrine gradually gained ground, and at present it is all but generally adopted. While some phenomena, as the absorption and refraction of light, are even yet obscurely explained by either theory, others, especially the phenomena of interference and polarized light, are wholly inexplicable by the corpuscular, and receive a most lucid explanation by the undulatory theory. On this ground the former is considered untenable, and the latter alone suitable to the present condition of science. But to enter at length into this argument would be so foreign to the design of this treatise that the reader is referred to Pouillet's *Elémens de*

Physique, Young's Essays, Airy's Tracts, 2nd edition, and Herschel's article on Light in the Encyclopædia Metropolitana.

I shall now, however, state the laws of light in the ordinary language, which is founded on the corpuscular theory, and analogous to that which has been employed in treating of heat.

Diffusion of Light.—Light emanates from every visible point of a luminous object, and is equally distributed on all sides if not intercepted, diverging like radii drawn from the centre to the circumference of a circle. Thus, if a single luminous point were place in the centre of a hollow sphere, every point of its concavity would be illuminated, and equal areas would receive equal quantities of light. The smallest portion of light which can be separated from contiguous portions is called *a ray of light.* Each ray when not interrupted in its course, and while it remains in the same medium, moves in a straight line; as is obvious by the appearance of shadows cast by the side of a house, or of a sunbeam admitted through a small aperture into a dark room. Owing to these modes of distribution, it follows that the quantity of light which falls upon a given surface decreases as the square of its distance from the luminous object increases, the same law which regulates the heating power of a hot body.

The passage of light is progressive, time being required for its motion from one place to another. By astronomical observations it is found that light travels at the rate of nearly 195,000 miles in a second of time, and would require about eight minutes to pass from the sun to the earth. Owing to this prodigious velocity, the light caused by the firing of a cannon or a sky-rocket is seen by different spectators at the same instant, whatever may be their respective distances from the rocket, the time required for light to travel 100 or 1000 miles being inappreciable to our senses.

When light falls upon any body, it may, like radiant heat, dispose of itself in three different ways, being *reflected*, *refracted*, or *absorbed.* The phenomena connected with the two former modes of distribution I shall proceed to consider in succession; while those of absorbed light will be included under the head of *Decomposition of Light.*

REFLECTION OF LIGHT.

Light may be reflected by all media, whether solid, liquid, or gaseous, when it passes from one medium into another of a different nature or density; but there is great difference in the power of reflection. Bright metallic surfaces, such as polished brass and silver, or clean mercury, reflect nearly all the rays which fall upon them; while those which are dull and rough reflect but few. The reflection of light, like that of heat, takes place at the surface of bodies, and appears influenced rather by the condition of the surface than by the nature of the reflecting body. The direction of the reflected ray, whatever may be the nature or figure of the reflecting surface, is regulated by these two laws.

I. The incident and reflected rays always lie in the same plane, which plane is perpendicular to the reflecting surface.

II. The incident and reflected rays always form equal angles with the reflecting surface; or, what amounts to the same, the angle of incidence is always equal to the angle of reflection.

Hence, if the reflecting surface be a plane mirror, the direction of the reflected ray, being known, gives us that of the incident ray ; and *vice versâ*.

These laws apply equally to curved reflecting surfaces, whether convex or concave. As a curve may be viewed as a polygon with very short sides, it follows, from obvious mathematical considerations, that parallel rays, falling on a convex mirror, are scattered or made to diverge; while if they fall on a concave mirror they are concentrated, or made to converge into its focus. On the same principle it is plain that divergent rays, falling on a convex surface, are rendered parallel by reflection; and that rays diverging from the focus of a concave mirror on its surface, are also reflected in parallel lines.

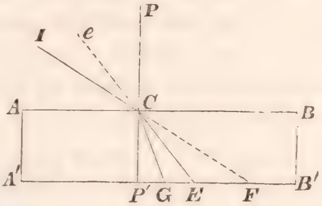
When the concave mirror is spherical, the parallel rays falling on it are not strictly collected into one point or focus ; this only happens when the mirror is accurately parabolic. Hence, if a luminous body be placed in the focus of one parabolic reflector, the rays which it gives off are all collected in the focus of a second parabolic reflector placed opposite to the first.

On these principles are constructed the reflecting telescope and the reflecting microscope; but this treatise is not the place for a description of these useful instruments.

REFRACTION OF LIGHT.

Light traverses the same transparent medium, such as air, water, or glass, in a straight line, provided no reflection occurs, and there is no change of density ; but when it passes from one medium into another, or from one part of the same medium into another of a different density, a change of direction always ensues at the plane of junction of the media, except when the ray is perpendicular to that plane. For instance, let AB A′B′, fig. 1, represent a vertical section of a vessel full of water, and PP′ the perpendicular to the surface of the water at the point C. Should a ray of light enter the water perpendicularly to its surface, as in the line of PC, it will continue on its course to P′ without deviation; but if it descend obliquely, as in the direction of IC, it will suffer a bend at C, and proceed to E, instead of advancing along the dotted line to F. Conversely, were a ray of light to emanate from E and emerge at C, it would not advance to *e*, but take the direction of CI. By comparing the direction of the refracted ray in these two cases in relation to the vertical PP′, it will be seen that the ray approaches the perpendicular in entering from air into water, and recedes from it in passing out of water into air. The same remark applies to the passage of light from or into air into or out of solid or liquid media in general.

Fig. 1.



Bodies differ in their power of refracting light. In general, the denser a substance is, the greater is the deviation which it produces. If in fig. 1 sulphuric acid were mixed with the water, the ray IC would be refracted to some point between E and G; and if a solid cake of glass were substituted for that liquid, the refracted ray would be bent down to CG. But this is far from universal:—alcohol, ether, and olive oil, which are lighter than water, have a higher refractive power. Observation has shown it to be a law, to which no exception is yet known, that oils and other highly inflammable bodies, such as hydrogen, diamond, phosphorus, sulphur, amber, olive oil, and camphor, have a refractive power which is from two to seven times greater than that of incombustible substances of equal density. But whatever may be the refractive power of bodies in relation to each other, refraction is always governed by the two following laws, discovered in 1618 by Snell, though usually ascribed to Descartes.

1. The direction of the incident and refracted ray is always in a plane perpendicular to the surface common to the media.

2. The sine of the angle of incidence and the sine of the angle of refraction are in a constant relation for the same media.

The sine of the angle of refraction being taken = 1, the sines of the angles of incidence in different substances may thus be referred to a common measure or unit of comparison. In common flint glass the ratio is nearly as 1·6 to 1; in water, as 1·336 to 1. The numbers representing the sines of the angles of incidence are called the *indices of refraction,* and indicate the degree of refractive power. Thus, the index of refraction of flint glass is 1·6; that of water, 1·336; that of the diamond, 2·755.

Subjoined is a table of the refractive indices of gases, that of a vacuum being unity.

Name of Gas.	Ref. Index.	Name of Gas.	Ref. Index.
Oxygen	1·000272	Carbonic Oxide	1·000340
Hydrogen	1·000138	Carbonic Acid	1·000449
Nitrogen	1·000300	Hydrochloric Acid	1·000449
Chlorine	1·000772	Ammonia	1·000385
Protoxide of Nitrogen	1·000503	Cyanogen	1·000834
Binoxide of Nitrogen	1·000303	Hydrocyanic Acid	1·000451
Olefiant Gas	1·000678	Sulphurous Acid	1·000665
Marsh Gas	1·000443	Hydrosulphuric Acid	1·000644
Ether Vapour	1·001530	Bisulphuret of Carbon Vapour	1·001500

In studying the influence of curved media on light on the same principles as have been applied to reflection by curved mirrors, it is found that convex lenses act like concave mirrors, and collect the refracted rays into a focus; while concave lenses, like convex mirrors, cause the rays to diverge. The properties of convex lenses are, therefore, extensively applied in the construction of the refracting telescope, which is the kind most commonly employed, and of the refracting microscope.

A convex lens fitted into the wall of a darkened chamber constitutes the arrangement of a *camera obscura*, the inverted images of external objects being received on a disk of paper or a white board. In the simple telescope the lens is placed at the extremity of a tube of such length that the image may be formed within the tube, and the observer looks from the other end at the image formed in the air. The eye acts on the same principle. Luminous rays entering the transparent parts of the eye are refracted by the cornea and crystalline lens, and are brought into a focus at the bottom of the eye, an inverted image of external objects being formed upon the retina as on the table of a camera obscura. For distinct vision it is necessary that this image should be formed exactly on the retina. Hence, were the eye an ordinary lens, having an invariable focus, our range of vision would be very narrow; an eye fitted for seeing at a distance would be useless for near objects; and persons who could see near objects would be blind to remote ones. Two rays emanating from a distant point cannot *both* fall upon so small an object as the eye, unless they are nearly parallel; for if they diverged by even a very small angle, they would, before reaching the eye, separate by an interval exceeding the diameter of the cornea. On the contrary, rays in rapid divergence may enter the eye, provided the point from which they emanate be close to it ; and the nearer the object, the more divergent the rays which enter. When, therefore, we observe a distant landscape, then successively notice nearer and nearer objects, and lastly cast the eyes upon the page of a book only six inches distant, we receive rays coming from a multitude of different objects, each set of rays having its own peculiar divergence, and requiring a separate focus ; and yet, so wonderful is the adjusting power of the eye, a single minute suffices for distinctly seeing all the objects so beheld, without the consciousness of an effort.

The adjustment of the eye for different distances appears to depend on a power of increasing or decreasing the distance between the posterior part of the eye and the lens ; though the mechanism by which this is accomplished is unknown. Some ascribe it to a change in the figure of the whole eye-ball, produced by the muscles which move the eye ; but Brewster, I think with better reason, considers the position of the lens to be varied by the same contractile tissue which determines the movements of the iris and the size of the pupil. To this adjusting power, however, there is a limit. The distance at which most persons see small objects distinctly is about six inches : at shorter distances the rays are so divergent, that their focal point falls behind the retina, and indistinct vision is the consequence. Persons called *long-sighted* are unable to see near objects distinctly, owing to a weak refracting power of the eye, due to deficient convexity or density in the humours of the eye. This is the infirmity of advancing life, and is remedied by convex glasses, which cause diverging rays to be parallel or slightly convergent. In *short-sighted* persons the refractive power, either from undue convexity or undue density of the cornea and lens, is so powerful, that all rays which do not diverge rapidly are brought to a focus before they reach the retina. Youth is the period most obnoxious to this imperfection, and assistance is derived from a concave glass, which causes parallel rays to diverge, and thereby counteracts the refracting influence of the eye.

Since the rays which fall on a convex lens from any object are divergent, and are collected into a focus behind the lens, it follows that the image there formed must be inverted, the rays from the top of the object forming the lower part, in point of position of the image. Yet the eye sees objects erect. This remarkable fact has not yet been satisfactorily explained. It has been supposed by some that in infancy we actually see objects inverted, and only discover that they are not so by the correction derived from experience; but this fallacy has been fully corrected by observation on persons born blind, who first obtained the power of vision when of an age to describe what they saw.

Double Refraction.—If on a piece of paper with a black line on its surface we place a rhombohedron of Iceland-spar, and then look at the line through the crystal, it will be found that in a certain position the line appears single as when seen through water or glass; but in other positions of the crystal two lines are visible parallel to each other, and separated by a distinct interval. The light in passing through the crystal is divided into two portions, one of which obeys the laws of refraction already explained (page 57); whereas the other portion proceeds in a wholly different direction, and hence gives the appearance of two objects instead of one. The former is termed the *ordinary*, the latter the *extraordinary* ray. This phenomenon is known by the name of *double refraction,* and has been witnessed in many crystallized substances, as in minerals and artificial salts.

Light transmitted through Iceland-spar or other doubly refracting substances, is found to have suffered a remarkable change. In this state it is distinguished from common light by the circumstance, that when it falls upon a plate of glass at an angle of 56° 11′, it is almost completely reflected in one position of the glass, and is hardly reflected at all in another: if reflected when the plane of reflection is vertical, no reflection ensues when the reflecting plane is horizontal, the incident angle being maintained at 56° 11′. This curious property, so different from common light, has been theoretically ascribed to a kind of *polarity* of such sort, that each side of a ray of light is thought to have a character different from the two adjacent sides at right angles to it; and hence the origin of the term *polarized light*, by which this property is ditinguished. Light is polarized by reflection from many substances, such as glass, water, air, ebony, mother-of-pearl, and many crystalized substances, provided the light is incident at a certain angle peculiar to each surface, and which is called the *polarizing angle.* Thus, the polarizing angle for glass is 56° 11′, and for water 53° 14′; that is, common light reflected by glass and water at the angles stated will be polarized.

The recent very interesting researches of Faraday (see Phil. Mag. 1845 and 1846), have demonstrated that the transmission of light through transparent bodies is affected by the magnet. Thus, when a ray of polarized light is made to traverse certain kinds of glass, and certain fluids placed in the axis of a spiral conveying an electric current, and consequently a temporary magnet, or when the line of magnetic action between the poles of a powerful magnet is made to coincide with the direction of a ray of polarized light, the plane of polarization is made to rotate to the right or to the left, according as the current passes from the circumference to the centre, or *vice versâ*.

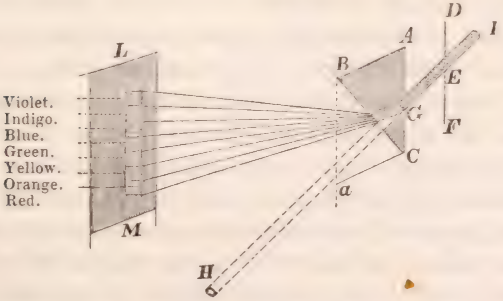
It was at first supposed, when this discovery was announced, that the ray of light had been directly acted on by the magnetic attraction, but the publication of Faraday's very striking researches shows that the light is only secondarily affected, the magnetic current causing a change in the molecular arrangement of the body through which the light is transmitted, in consequence of which, as by the action of heat, &c., the plane of polarization is made to rotate. For details the reader is referred to the original papers of Faraday, above cited.

The phenomena of double refraction and polarized light constitute a department of optics of great and increasing interest; but it is too remote from the pursuits of a chemical student to be treated of at length in this work. Those interested in such studies will find an excellent guide in Brewster's Treatise on Optics in the Cabinet Cyclopedia.

DECOMPOSITION OF LIGHT.

The analysis of light may be effected either by refraction or absorption. Newton, who discovered the compound nature of solar light, effected its decomposition by refraction, employing a solid piece of glass bounded by three plane surfaces, well known under the name of the *prism*. His mode of operating consisted in admitting a ray of light, IG, fig. 2, into a dark chamber through a window-shutter DEF, and interposing the prism ACB, so that the ray should pass obliquely through two surfaces, and be refracted by both. On receiving the refracted ray upon a piece of white paper LM, there appeared, instead

Fig. 2.



of a spot of white light, an oblong coloured surface composed of seven different tints, called the *prismatic* or *solar spectrum*. On subjecting each of these colours to refraction no further separation was accomplished; but on causing the rays separated by one prism to pass through a second of the same power and in an inverted position C B *a*, the seven colours disappeared, and a spot of white light appeared at H, in the very position which it would have occupied had both prisms been absent. From such and similar experiments Newton inferred that white light is a mixture of seven *colorific* rays—red, orange, yellow, green, blue, indigo, and violet; and that the separation of these primary or simple rays depended on an original difference of refrangibility, violet being the most refrangible and red the least so.

Though a prism is the most convenient instrument for decomposing light, the separation of the coloured rays is more or less effected by refracting media in general. Lenses, accordingly, disperse the colorific rays at the same time that they refract them; and this effect constitutes one of the greatest difficulties in the construction of telescopes, in so much as the separation or *dispersion*, as it is termed, of these rays diminishes the distinctness of the image. The combinations by which the defect is remedied are called *achromatic*.

Newton's analysis of light led him to explain the origin of the colours of natural objects. Of opaque bodies those are black which absorb all the light that falls upon them, and those white which reflect it unchanged: the various combinations of tints are the consequence of certain rays being absorbed, while those alone whose intermixture produces the observed colour are reflected. The same applies to transparent media, which are colourless like pure water when the light passes through unchanged, but are coloured when some rays are transmitted and others absorbed. This absorption of certain rays by coloured media, such as glass of different tints, affords another mode of decomposing light; and Brewster has ingeniously applied it to analyse the seven colours which compose the prismatic spectrum. He has proved by such experiments, what has been maintained before, that the seven colours of the spectrum are occasioned not by seven, but by three simple or primary rays; namely, the red, yellow, and blue. These rays are concentrated in those parts of the spectrum where each primary colour respectively appears; but each spreads more or less over the whole spectrum, the mixture of red and yellow giving orange, of yellow and blue green, and red with blue and a little yellow causing the violet.

The prismatic colours, according to the experiments of Sir W. Herschel, differ in their illuminating power: the orange illuminates in a higher degree than the red, the yellow than the orange. The maximum of illumination lies in the brightest yellow or palest green. The green itself is almost equally bright with the yellow; but beyond the full deep green the illuminating power sensibly decreases. The blue is nearly equal to the red, the indigo is inferior to the blue, and the violet is the lowest on the scale. (Phil. Trans. 1800.)

Calorific rays in Light.—The solar rays, both direct and diffused, are capable of exciting heat. When reflected or transmitted, no such effect results: the concave reflector and burning-glass remain cool, though intense heat is developed at their foci; and the atmosphere is not heated by the solar rays to which it gives a passage. But opaque bodies which absorb light are invariably heated by it, and the temperature is proportional to the absorbent power. Hence, dark-coloured substances, which are more absorbent than light ones, become hotter when exposed to sunshine. This is attested by the general preference given to light-coloured clothing during summer. Hooke, and subsequently Franklin, proved the fact by exposing pieces of cloth of the same texture and size, but different colours, upon snow to sunshine; when the snow under the dark specimens was found to melt more freely than under the light ones, the effect being nearly proportional to the depth of shade. Davy arrived at similar results. The coloured rays of the spectrum differ in heating power. This is shown generally by looking at the sun through glass of different colours, when it will be found that red and yellow glasses heat and oppress the eye much more than blue or green ones; but the fact was first rigidly demonstrated by Sir W. Herschel, by placing the bulb of a delicate thermometer in the coloured spaces of the solar spectrum. He found that it stood highest in the red space, fell lower and lower when successively removed towards the violet, and was lowest in the violet space. (Phil. Trans. 1800.)

The foregoing facts are explicable on the suppositions either that light is convertible into heat by absorption, or that heat is merely associated with light, and is absorbed along with it. Herschel maintained the latter view, and founded it on his observation that, though the red space of the spectrum is hotter than the other coloured spaces, there is a spot a little beyond the red, where little or no light appears, where the thermometer is higher than in the red itself. He hence inferred that there exists in the solar beam a distinct kind of ray, which causes heat but not light; and that these rays, from being less refrangible than the luminous ones, deviate in a smaller degree from their original direction in passing through the prism.

All succeeding experimenters confirm the statement of Herschel, that the prismatic colours differ in heating power; but they do not agree as to the spot where the heat is greatest. Englefield, Davy, and others affirmed with Herschel that it is beyond the red ray; while others, and in particular Leslie, contended that it is in the red itself. The observations of Seebeck (Edin. Journ. of Science, i. 358) explained these contradictory statements, by showing that the point of greatest heat varies with the kind of prism which is employed for forming the spectrum. When he used a prism of fine flint-glass, the greatest heat was uniformly beyond the red; with a prism of crown-glass, the red itself was the hottest part; and with a prism externally of glass, but containing water within, the maximum heat was neither in the red itself, nor beyond it, but in the yellow. These experiments have been confirmed by Melloni, who has succeeded with a prism of rock-salt in separating the spot of maximum heat from the coloured part of the spectrum by a much greater interval than had been done previously, and dissipating all remaining doubt as to the existence in solar light of calorific rays distinct from those rays which produce colour. As in simple radiant heat, there exist in solar light calorific rays of different characters, some being more, some less, refrangible. The former are proportionally less absorbed by feebly diathermanous media than the latter; whereas good diathermanous media absorb the less refrangible more freely than the more refrangible rays. For instance, the heat of the violet passes through water more readily than that of the yellow space, that of the yellow than the red; but in employing media always rising in transcalency, as crown-glass, flint-glass, and rock-salt, the obstruction to the least refrangible calorific rays continually decreases. Hence, in successively taking prisms of rock-salt, flint-glass, crown-glass, and water, the spot of greatest heat will be found first far beyond the red, then nearer the red, then in the red itself, and lastly in the yellow space of the spectrum. On using a prism still less transcalent than water, the maximum heat would be found on the violet side of the yellow space. By causing light, terrestrial as well as solar, to pass first through water, and then through glass coloured green by oxide of copper, Melloni so effectually absorbed all the calorific rays, that the issuing light did not affect the most delicate thermoscope. It would hence follow, not merely that light is associated with calorific rays quite distinct from the luminous rays, but that the latter contributes nothing to the heat evolved during the absorption of light.

Chemical rays.—Solar light is capable of producing powerful chemical changes. One of the most striking instances of it is its power of darkening the white chloride of silver; an effect which takes place slowly in the diffused light of day, but in the course of two or three minutes by exposure to sunshine. This effect was once attributed to the influence of the luminous rays; but Ritter and Wollaston traced it to the presence of certain rays that excite neither heat nor light, and which, from their peculiar agency, are termed *chemical* rays. The greatest chemical action is exerted just beyond or at the verge of the violet part of the prismatic spectrum; the spot next in energy is the violet itself; and the property gradually diminishes in advancing to the green, beyond which it seems wholly wanting. It hence follows that the chemical rays are still more refrangible than the luminous, in consequence of which they are dispersed in part over the blue, indigo, and violet, but in the greatest quantity at the extreme border of the latter.

The Daguerréotype, as well as Mr. Talbot's method of Photography, is founded on the action of the chemical rays of certain substances. The iodide of silver, formed by exposing a plate of silver to the vapour of iodine, is the substance used in the Daguerréotype. The chloride, iodide, and bromide of silver, formed on the surface of paper in a thin and uniform layer, are the bases of Talbot's method. The delicacy and beauty of the images produced in the Daguerréotype, however, far surpasses anything that has hitherto been produced on paper. For details on this subject, the student is referred to a little treatise by M. Arago, which has been translated into English.

Magnetizing rays.—The more refrangible rays of light were once thought to possess the property of rendering steel and iron magnetic; but since the experiments of Riess and Moser, this may be considered doubtful. (Brewster's Journal, II. 225.) The recent researches of Baron Reichenbach seem to indicate the presence of rays having a peculiar action on the animal system; and like the supposed magnetic rays, these are found among the more refrangible rays.

TERRESTRIAL LIGHT.

Under this head is included all kinds of artificial light. The common method of obtaining such light is by the combustion of inflammable matter, which gives out so much heat that the burning substance is rendered luminous in the act of being burned. All bodies begin to emit light when heat is accumulated within them in great quantity; and the appearance of glowing or shining, which they then assume, is called *incandescence.* The temperature at which solids in general begin to shine in the dark is between 600° and 700°; but they do not appear luminous in broad daylight till they are heated to about 1000°. The colour of incandescent bodies varies with the intensity of the heat. The first degree of luminousness is an obscure red. As the heat augments, the redness becomes more and more vivid, till at last it acquires a full red glow. If the temperature still increase, the character of the glow changes, and by degrees it becomes white, shining, with increasing brilliancy as the heat augments. Liquids and gases likewise become incandescent when strongly heated; but a very high temperature is required to render a gas luminous, more than is sufficient for heating a solid body even to whiteness. The different kinds of flame, as of the fire, candles, and gas light, are instances of incandescent gaseous matter.

Artificial lights differ in colour, and accordingly exhibit different appearances when transmitted through a prism. The white light of incandescent charcoal, which is the principal source of the light from candles, oils, and the illuminating gases, contains the three primary colorific rays, the red, yellow, and blue. The dazzling light emitted by lime intensely heated, first proposed by Lieut. Drummond for the trigonometrical survey (Phil. Trans. 1830), and of late so successfully applied by Messrs. Cooper and Carey for their gas microscope, gives the prismatic colours almost as bright as in the solar spectrum. The light emitted by iron feebly incandescent consists principally of the red rays, as does the red light obtained by means of strontia and lithia; that from ignited boracic acid is such a mixture of the blue and yellow rays as constitutes green; and incandescent soda emits a yellow light almost wholly free from the rays which cause the red and blue colours.

Artificial light differs from solar light in containing heat in two states. It contains simple radiant heat like that radiated from a body not luminous, and which may be separated by transmission through a plate of moderately thick glass; but the light so purified still heats any body which absorbs it, possessing calorific rays associated with its luminous rays like those in solar light, and like them susceptible of refraction by transparent media. Thus, Daniell found that the rays from incandescent lime were concentrated by convex lenses, and set fire to phosphorus placed in the focus (Phil. Mag. N. S. II. 59). Agreeably to the researches of Melloni, artificial light contains different modifications of radiant heat, which not only differ in refrangibility, but in transmissibility through diathermanous media.

The chemical agency of artificial light is analogous to that from the sun. In general the former is too feeble for producing any visible effect; but light of considerable intensity, such as that from ignited lime, darkens chloride of silver, and seems capable of exerting the same chemical agencies as solar light, though in a degree proportionate to its inferior brilliancy. (An. of Phil. xxvii. 451.)

Light emanates from some substances either at common temperatures or at a degree of heat disproportioned to the effect, giving rise to an appearance which is called *phosphorescence*. This is exemplified by a composition termed *Canton's phosphorus*, made by mixing three parts of calcined oyster-shells with one of the flower of sulphur, and exposing the mixture for an hour to a strong heat in a covered crucible. The same property is possessed by chloride of calcium (Homberg's phosphorus), anhydrous nitrate of lime (Baldwin's phosphorus), some carbonates and sulphates of baryta, strontia, and lime, the diamond, some varieties of fluor-spar called *chlorophane*, apatite, boracic acid, borax, sulphate of potassa, sea-salt, and by many other substances. Scarcely any of these phosphori act unless they have been previously exposed to light, though they do not always shine with light of the same colour as that which excites the phosphorescence: for some, diffused daylight or even lamp-light will suffice; while others require the direct solar light, or the light of an electric discharge. Exposure for a few seconds to sunshine enables Canton's phosphorus to shine in a dark room for several hours afterwards. Warmth increases the intensity of light, or will renew it after it has ceased;—but it diminishes the duration. When the phosphorescence has ceased it may be restored, and in general for any number of times, by renewed exposure to sunshine; and the same effect may be produced by passing electric discharges through the phosphorus. Some phosphori, as apatite and chlorophane, do not shine until they are gently heated; and yet if exposed to a red heat, they lose the property so entirely that exposure to solar light does not restore it. Pearsall has remarked, that in these minerals the phosphorescence, destroyed by heat, is restored by electric discharges; that specimens of fluor spar, not naturally phosphorescent, may be rendered so by electricity; and that this agent exalts the energy of natural phosphori in a very remarkable degree. (R. Inst. Journal, N. S. i.) The theory of these phenomena is obscure. Chemical action is not the cause, for these phosphori shine *in vacuo* or in gases which do not act chemically on them, and some even under water. It may be presumed that light causes in them a certain vibratory state analogous to that, though in a far lower degree, which exists in incandescent matter.

Another kind of phosphorescence is observable in some bodies when strongly heated. A piece of lime, for example, heated to a degree which would only make other bodies red, emits a brilliant white light of such intensity that the eye cannot support its impression.

A third species of phosphorescence is observed in the bodies of some animals, either in the dead or living state. Some marine animals, and particularly fish, possess it in a remarkable degree. It may be witnessed in the body of the herring, which begins to phosphoresce a day or two after death, and before any visible sign of putrefaction has set in. Sea-water is capable of dissolving the luminous matter; and it is probably from this cause that the waters of the ocean sometimes appear luminous at night when agitated. This appearance is also ascribed to the presence of certain animalcules, which, like the glow-worm of this country, or the fire-fly of the West Indies, are naturally phosphorescent.

Light sometimes appears during the process of crystallization. This is exemplified by a tepid solution of sulphate of potassa in the act of crystallizing; and it has been likewise witnessed under similar circumstances in a solution of fluoride of sodium and nitrate of strontia. Another instance of the kind is afforded by the sublimation of benzoic acid. Allied to this phenomenon is the phosphorescence which attends the sudden contraction of porous substances. Thus, on decomposing by heat the hydrates of zirconia, peroxide of iron, and green oxide of chromium, the dissipation of the water is followed by a sudden increase of density suited to the changed state of the oxide, and a vivid glow appears at the same instant. The essential conditions are, that a substance should be naturally denser after decomposition than it was previously, and that the transition from one mechanical state to the other should be abrupt.

Instruments designed for measuring intensities of light are termed *photometers*. That of Leslie is the only one used to estimate the strength of the sun's light. It consists of his differential thermometer, with one ball made of black glass. The clear ball transmits all the light that falls upon it, and therefore its temperature is not affected; it is all absorbed, on the contrary, by the black ball, and by heating and expanding the air within, causes the liquid to ascend in the opposite stem. The whole instrument is covered with a case of thin glass, the object of which is to prevent the balls from being affected by currents of cold air. The action of this photometer depends on the absorption of the heat by which light is accompanied.

Leslie recommended his photometer also for determining the relative intensities of artificial light, such as that of candles, oil, or gas. This application of it differs from the foregoing, because light from terrestrial sources contains calorific rays of different properties; some being largely absorbed by glass, and others freely transmissible. The former, being for the most part arrested by the outer glass-case, will not cause any great error; but the latter must give rise to serious fallacies whenever the calorific and luminous rays of the two lights are not in the same ratio. This is rarely, if ever, the case with lights which differ in colour. Thus, the light emitted by burning cinders or red-hot iron, even after passing through glass, contains a quantity of calorific rays, which is out of all proportion to the luminous ones; and, consequently, they may and do produce a greater effect on the photometer than some lights whose illuminating powers are far stronger.

A photometer on a different principle has been described by Rumford in his Essays. It determines the relative strength of lights by a comparison of their shadows, and is susceptible of great accuracy when employed with the required care; but,* like the foregoing, its indications cannot be trusted when there is much difference in the colour of the lights. In this case, the best procedure is, to observe the distance from each light at which any given object, as a printed page, ceases to be distinctly visible. The illuminating power of the lights so compared is as the squares of their distances.

ON THE RELATIONS OF HEAT AND LIGHT.

Radiant heat and light have the most intimate resemblance. They are distributed, reflected, refracted, absorbed, transmitted, polarized, according to laws so exactly parallel, as to force on the mind the conviction that their causes are likewise similar. If light be due to ethereal vibrations, it is difficult not to assign a similar cause to radiant heat. The obstacle to adopting this view arises from the peculiar relations of heat to matter as connected with change of form, with specific heat, and with heat of temperature. The outline of such an undulatory theory might be thus stated:—Heat may be considered identical with the universal ether, so that the terms ether and matter of heat would apply to the same substance. Diffused within the pores of bodies this ether causes the condition of temperature, and in a state of more intimate union it determines their form. Conduction may be due to a peculiar vibration of ether, advancing slowly among the molecules of matter, and modified by their presence,—a radiation from particle to particle. Common radiation of heat may be ascribed, not to the ether itself being ejected from a hot body, but to ethereal impulses originating in the same manner as those of light, but having waves of different grades both of length and intensity. It would not be prudent, however, at present to embody such a theory with the ordinary doctrines of heat, though as a scientific speculation it is a subject of great and increasing interest.

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* See an Essay on the Construction of Coal Gas Burners, &c. in the Edinburgh Philosophical Journal for 1825.

SECTION III.

ELECTRICITY.

Elementary Facts.—When certain substances, such as amber, glass, sealing wax, sulphur, are rubbed with dry silk or cloth, they are found to have acquired a property, not observable in their ordinary state, of causing contiguous light bodies to move towards them; or if the substances so rubbed be light and freely suspended, they will move towards contiguous bodies. After a while this curious phenomenon ceases; but it may be renewed an indefinite number of times by friction. The principle thus called into action is known by the name of *electricity*, from the Greek word ηλεκτρον, amber, because the electric property was first noticed in it. The same term is applied to the science which treats of the phenomena of electricity.

When a substance by friction or any other means acquires the property just stated, it is said to be *electrified*, or to be *electrically excited;* and its motion towards other bodies, or of other bodies towards it, is ascribed to a force called *electric attraction.* But its influence, on examination, will be found to be not merely attractive; on the contrary, light substances, after touching the electrified body, will be disposed to *recede* from it just as actively as they approached it before contact. This is termed *electric repulsion.* By aid of the electrical machine, electric attraction and repulsion may be displayed by a great variety of amusing and instructive experiments, showing how readily an invisible power is called into operation, and how wonderfully inert matter is subject to its control. But the student may witness these effects quite satisfactorily by very simple apparatus. Let him suspend a thread of white sewing silk from the back of a chair so that one end may hang freely, taking the precaution to moisten that end slightly by holding it between the fingers, while the rest of the thread is carefully dried by the fire; and let him then place near the free end a piece of sealing wax previously rubbed on the sleeve of his coat. The silk will move towards it; but after touching the excited wax two or three times, it will recede from it.

When an electrified body touches another which is not electrified, the electric property is imparted by the former to the latter. Thus, on touching the free end of the suspended silk thread with the excited wax, the silk will itself be excited, as shewn by its moving towards a book, a knife, or other unexcited object placed near it. But although electricity is always imparted by an excited to an unexcited body by contact, the latter does not always exhibit electric excitement. If, for example, the suspended silk be wetted along its whole length, it will be strongly attracted by the excited wax, but after contact it will not evince the least sign of being itself electrified. Nevertheless, electricity is communicated to the silk in both cases; only it is retained by silk when dry, and is lost as soon as received by wet silk. Such observations led to the discovery that electricity passes with great ease over the surface of some substances, and with difficulty over that of others, and hence to the division of bodies into *conductors* and *non-conductors* of electricity. If electricity be imparted to one end of a conductor, such as a copper wire, the other extremity of which touches the ground, or is held by a person standing on the ground, the electricity will pass along its whole length and escape in an instant, though the wire were several miles long; whereas excited glass and resin, which are non-conductors, may be freely handled without losing any electricity except at the parts actually touched. To the class of conductors belong the metals, charcoal, plumbago, water, and aqueous solutions, and substances generally which are moist or contain water in its liquid state, such as animals and plants, and the surface of the earth. These, however, differ in their conducting power: of the metals, Harris found silver and copper to be the best conductors; and after these follow gold, zinc, platinum, iron, tin, lead, antimony, and bismuth (Phil. Trans. 1827). This order, as Forbes has remarked, is nearly that of their conducting powers for heat. Aqueous solutions of acids and salts conduct much better than pure water. To the list of non-conductors belong glass, resins, sulphur, diamond, dried wood, precious stones, earth, and most rocks when quite dry, silk, hair, and wool. Air and gases in general are non-conductors if dry, but act as conductors when saturated with moisture.

This knowledge is of continual application in electrical experiments. When it is wished to collect electricity on a metallic surface, the metal must be *insulated* that is cut off from contact with the earth, and with conductors touching the ground, by means of some non-conductor; an object commonly effected either by supporting it on a handle of glass, or by placing it on a stool made with glass feet. Another mode of insulating is to suspend a substance by silk threads. But such insulators must be dry; since they begin to conduct as soon as they grow damp, and conduct well, as in the experiment above described, when wet. Again, electrical experiments are very apt to fail in damp weather, because the moisture both carries off electricity directly, and (by being deposited on the glass supports) destroys the insulation.

To diminish this inconvenience it is usual to keep the insulators warm, and to coat them with a varnish made by dissolving the resin called shell-lac in alcohol, this resinous matter being much less prone to attract moisture from the air than glass. The same principles account for an error once prevalent, that a metal cannot be excited by friction: if held in the hand, indeed, it exhibits no sign of excitement when rubbed, because the electricity is carried off as soon as excited; but if, while carefully insulated, it is rubbed with a dry cat's fur, excitement readily ensues.

On comparing the electric properties manifested by glass and sealing wax when both are rubbed by a woollen or silk cloth, they will be found essentially different; hence it is inferred that there are two kinds or states of electricity, one termed *vitreous*, because developed on glass, and the other *resinous* electricity from being first noticed on resinous substances. These two kinds of electricity, one or other of which is possessed by every electrical substance, are also termed *positive* and *negative*, the terms *vitreous* and *positive* being used synonymously, as are *resinous* and *negative*: they are also denoted by the signs + and —. If two electrified substances are both positive or +, or both negative or —, they are invariably disposed to recede from each other, that is, to exhibit electric repulsion; but if one be +, and the other —, their mutual action is as constantly attractive. The end of a silk thread, after contact with an electrified stick of sealing-wax, is repelled by the wax, because both are —; but a dry warm wine glass, if rubbed with cloth or silk, will be +, and if then presented to the thread, attraction will ensue, A silk thread in a *known* electric state, thus indicates the kind of electricity possessed by other substances: a convenient mode of doing this is, to draw a thread of white silk rapidly through a fold of coarse brown paper previously warmed, by which means its whole length will be rendered +.

When two substances are rubbed together so as to electrify one of them, the other, if in a state to retain electricity, will be excited also, one being always —, and the other +. It is easy to be satisfied of this by very simple experiments. Rub a stick of sealing-wax on warm coarse brown paper, and the paper will be found to repel a positively excited thread of silk, while the wax will attract it; if a warm wine glass be rubbed on the brown paper, the glass will be +, as shown by its repelling the + thread, while the same thread will be attracted by the — paper; friction of sealing wax on a silk riband renders the wax — and the riband +, but with glass the riband is —. If two silk ribands, one white and the other black, be made quite warm, placed in contact, and then drawn quickly through the closed fingers, they will be found on separation to be highly attractive to each other, the white being +, and the black —. The back of a cat is + to all substances with which it has been tried, and smooth glass is + to all except the back of a cat. Sealing wax is — to all the substances just enumerated, but becomes + by friction with most of the metals. The reader will perceive from these facts that the same substance may acquire both kinds of electricity, becoming + by friction with one body, and — with another.

THEORIES OF ELECTRICITY.

The nature of electricity, like that of heat, is at present involved in obscurity. Both these principles, if really material, are so light, subtile, and diffusive, that it has hitherto been found impossible to recognise in them the ordinary characteristics of matter; and therefore electric phenomena may be referred, not to the agency of a specific substance, but to some property or state of common matter, just as sound and light are produced by a vibrating medium. But the effects of electricity are so similar to those of a mechanical agent—it appears so distinctly to emanate from substances which contain it in excess, and rends asunder all obstacles in its course so exactly like a body in rapid motion, that the impression of its existence as a distinct material substance *sui generis* forces itself irresistibly on the mind. All nations, accordingly, have spontaneously concurred in regarding electricity as a material principle; and scientific men give a preference to the same view, because it offers an easy explanation of phenomena, and suggests a natural language easily intelligible to all.

Theory of two Electric Fluids.—This theory, the fundamental facts of which were supplied partly by Dufay, and partly by Symmer, is founded on the assumed existence of two electric fluids, which Dufay distinguished by the terms *vitreous* and *resinous* electricity. In order to account for electric phenomena, by this supposition, the two fluids are assumed to possess the following properties:—They are both equally subtile and elastic, universally diffused and therefore present in all bodies possessed of the most perfect fluidity, each highly repulsive to its own particles, and as highly attractive to those of the opposite kind, these attractive and repulsive forces being exactly equal at the same distance, and both varying inversely as the square of the distance varies. Electric quiescence is ascribed to these fluids being combined and neutralized with each other; and electric excitation is the consequence of either fluid being in excess. Their combination is destroyed by several causes, of which friction is one.

This theory, as commonly stated, takes little or no cognizance of any attraction between the electric fluids and other material substances. But it would be against all analogy to suppose no such influence to exist; and indeed the supposition of an attractive force acting at insensible distances seems necessary to account for the impediment caused by non-conductors to the free movement of the electric fluids.

Theory of a single Fluid.—The celebrated American philosopher, Franklin, proposed a different theory, founded on the supposition of a single electric fluid, the particles of which are conceived to repel each other with a force diminishing as the squares of the distance, and to be attracted by matter in general according to the same law. Material substance in its unelectric state is regarded as a compound of electricity and matter, saturated and neutralized with each other. It is also an assumption, shown to be necessary by Æpinus and Cavendish, that ponderable bodies repel each other with the same force and according to the same law as the particles of electricity. From the nature of these postulates it will be easy to anticipate their application. Unelectric bodies are such as have their natural quantity of electricity, which precisely suffices to saturate and neutralize the matter of which they consist. They are then electrically indifferent; because the repulsion exerted between the electricity and matter of contiguous bodies is exactly counteracted by the attraction of the electric fluid in each for the matter of the other. Electrical excitement is occasioned either by increase or diminution of the natural quantity of electricity. These opposite states are denoted by the algebraic terms *positive* and *negative;* the former corresponding to the vitreous, the latter to the resinous electricity of Dufay.

To the theory of Franklin it is usually objected that it involves an assumption at variance with the laws of gravitation, namely, that of matter being repulsive to itself; but this objection is unfounded, as the laws of gravitation have been investigated for matter only when in its ordinary state, and probably do not apply in cases of electric excitement. The researches of Mossotti on the forces which regulate the internal constitution of bodies amply justfy this conclusion. Adopting with Franklin a single electric fluid, he has shown that gravitation is perfectly consistent with the supposition that the molecules of matter are repulsive to each other. He has supported this opinion by a mathematical investigation of the conditions of equilibrium both for the molecules of matter and for the electric fluid. The results at which he arrived show that two molecules of matter surrounded by their electric atmospheres, are mutually attractive when separated by a sensible distance ;—that the attraction increases on the approach of the atoms up to a certain point, where the attractive force attains its maximum, and beyond which the molecules are mutually repulsive. In this manner, gravitation, cohesion, and the resistance of matter to compression, are attributed to the same forces. These views certainly afford a happy explanation of the molecular mechanism ; but as they have not yet been sufficiently tested, I shall retain the theory of the two electricities, which was adopted in former editions, substituting however, agreeably to present usage, the terms positive and negative, for vitreous and resinous electricity.

CAUSES OF ELECTRIC EXCITEMENT.

Friction.—This cause of electric excitement having been already mentioned, it here only remains to state the usual modes of developing electricity by friction. A supply of negative electricity is easily obtained by rubbing a stick of sealing-wax, or a glass tube covered with sealing-wax, with silk or woollen cloth ; and positive electricity is freely developed when a dry glass tube is rubbed with silk, brown paper, or flannel, the surface of which is covered with a little amalgam. But for obtaining an abundant supply of electricity it is necessary to employ an electrical machine, which is a mechanical contrivance for exposing a large surface of glass to continuous friction. As now constructed, it is formed either with a cylinder or plate of glass which is made to revolve upon an axis, and pressed during rotation by cushions or rubbers made of leather stuffed with flannel, and covered usually with silk. On the rubber is spread an amalgam of tin and zinc, rendered adhesive by admixture with a small quantity of lard or tallow. To prepare the amalgam, melt in a Hessian crucible one ounce of tin and three of zinc, then add two ounces of mercury heated to near its boiling point, stir briskly with a stick for a few minutes, and pour the mixture on a clean dry stone : when cold, pulverize and sift, and preserve the fine powder in a well-corked dry phial. Another essential part of the machine is the *prime conductor*, which is an insulated conductor, commonly made of brass, placed in such immediate proximity to the revolving glass, that the electric state of the one is instantly imparted to the other.

The electricity developed by the electrical machine is due partly to friction, which disunites the combined electric fluids of the glass and rubber, but principally to the oxidation of the amalgam. The positive fluid accumulates in the glass, and passes from it to the prime conductor, while the negative fluid accumulates in the rubber and its conductor. But to keep up the supply of electricity, the rubber must be connected with the ground, so that its — fluid may escape; or if we wish to obtain — electricity from the rubber, the prime conductor should communicate with the ground, that its + fluid may escape.

Change of temperature.—The operation of this cause of electric excitement was first noticed in certain minerals, such as tourmalin and boracite, not possessed of that symmetric arrangement of parts commonly observed in crystals, and which are electrified by the application of heat. But a far more general principle was detected by Seebeck, who found that the electric equilibrium is disturbed in certain metallic rods or wires when one extremity has a different temperature from that of the other, whether the difference be effected by the application of heat or cold. This observation has been since shown by Cumming to be true of all metals (An. of Phil. N. S. v. 427); and the same subject has been examined by Prideaux (Phil. Mag. and An. iii.). The experiment is usually made by heating or cooling the point of junction of two metallic wires, which are soldered together; but Becquerel has proved that the contact of different metals is not essential. (An. de Ch. Ph. xli. 353.)

Chemical action.—Another, and perhaps by far the most fertile, source of electricity is chemical action. This was strongly denied by Davy, in his Bakerian lecture for 1826; but the experiments of Becquerel, De la Rive, and Pouillet, afford decisive proof that chemical union and decomposition are both attended with electrical excitement (An. de Ch. et Ph. vol. xxxv. xxxvi. xxxvii. xxxviii. and xxxix.).

Contact.—Another reputed source of electricity is contact of different substances, especially of metals; a source originally suggested by Volta, who founded on it a theory of galvanism. Volta stated that clean plates of zinc and copper, insulated by glass handles, became electric by being made to touch each other, and then separated. When the zinc alone was insulated, it became +, and when the copper alone was insulated, it became —. But the quantity of electricity thus developed is confessedly so small as to require the most delicate instruments to detect it; and the experiments of De la Rive

(An. de Ch. et Ph. xxxix. 297; lxii. 147), and those of Parrot (ibid. xlvi. 361), have shown, in a manner apparently decisive, that the electricity developed in such experiments is derived either from a slight degree of chemical action, or from friction; and that contact alone, if unattended by chemical action or by friction, produces not the least excitement of electricity. I apprehend, therefore, that the facts adduced by Volta must be rejected.

Changes of form.—The changes of form caused in a substance by variations of temperature, such as liquefaction and solidification, the formation and condensation of vapour, constitute another reputed source of electricity. Pouillet, however, questions this opinion; and maintains, that in every case where change of form produces electric excitement, there is also chemical action. Thus, when water evaporates, the electricity is due to the separation of the water from its saline impregnations, or to its action on the containing vessel; and pure water, evaporated in platinum vessels, produces no excitement. He ascribes to the separation of water from saline matter, constantly going on at the surface of the earth, and to the chemical changes produced in the growth of vegetables, the development of a great part of the atmospheric electricity. My own experiments have given similar results; but Harris, with an apparatus of great delicacy, has detected electricity during the evaporation of pure water in platinum vessels, although in very small quantity.

Proximity to an electrified body.—It is a direct consequence of the attractive and repulsive powers ascribed to the electric fluids, that an unelectrified conductor must be excited by the vicinity of an electrified body. The opposite ends of the conductor are oppositely electrified, and in an equal degree: the excitement is found, as would be anticipated, to be greatest at the extremities, and to diminish gradually towards the middle line, which is neutral. The electricity thus developed by the contiguity of an electrified body is said to be *induced*, or to be excited by *induction*.

The student should reflect carefully on these inferences from the theory of electricity, since the applications of such knowledge are numerous. A few of these may now be enumerated:—

1. An electrified body attracts light objects near it, because it induces in them a state opposite to itself. The attention is most lively when the light object is a conductor, and in contact with the ground, since it then more completely assumes an electric state opposed to that of the inducing body. A non-conductor is very imperfectly electrified by induction, because the electric fluids cannot quit each other from inability to move through the non-conductor.

2. If a stick of sealing-wax, strongly — be presented to a thread or pith ball which is also negatively, but feebly, excited, repulsion will ensue at a considerable distance, followed by attraction when the distance is small. This attraction is due to the strongly excited wax acting by induction on the feebly — thread, thereby causing it to have an access of + electricity.

3. The + electricity collected on the prime conductor of an electrical machine is by some ascribed, not to a transfer of that fluid from the glass to the prime conductor, but to a part of the combined electricities of the prime conductor being separated by induction, and the — fluid being imparted to the + glass. The same view is applicable to any system of conductors in contact with the prime conductor, as also to conductors connected with the rubber. It is difficult to say which explanation is the more correct, or whether both may not be true.

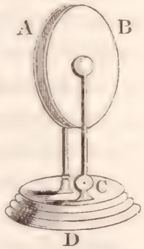
4. On moving the hand towards the prime conductor of an excited electrical machine, the hand becomes — by induction, and the spark ultimately obtained restores the equilibrium. In like manner a negatively electrified cloud renders + a contiguous tree or tower, and then a stroke of lightning follows as a consequence of attraction between the two accumulated fluids.

5. The action of the *Leyden jar* depends on the principle of induced electricity. A glass jar or bottle with a wide mouth is coated externally and internally with tinfoil, except to within three or four inches of its summit; and its aperture is closed by dry wood or some imperfect conductor, through the centre of which passes a metallic rod communicating with the tinfoil on the inside of the jar. On placing the metallic rod in contact with the prime conductor of an excited electrical machine, while the outer coating communicates with the ground, the interior of the jar acquires a charge of + electricity, and the exterior becomes as strongly —. The exterior may be handled without destroying the charge, provided no communication be at the same time made with the interior. But when a conductor communicates with both surfaces at the same instant, the two fluids rush together with violence, and the equilibrium is restored. Whether in this and similar cases the two fluids coalesce entirely on the intermediate conductor, or whether each from its velocity may not in part pass the other, and be projected to the opposite surface, is a question on which electricians are not agreed.

The Leyden jar affords the means of passing through bodies a large quantity of electricity. For not only may jars of any required size be employed, but it is easy so to arrange any number of such jars, that they shall all be charged and discharged at the same time, constituting what is termed an *electrical battery*. The arrangement is made by placing a number of Leyden jars in a box lined with tinfoil, by which means their outer surfaces have free metallic communication with each other, and connecting their inner surfaces by wires.

6. The principle of induced electricity was ingeniously applied by Volta in the construction of the *Condenser*. This apparatus, fig. 1, consists of two brass plates, A and B, supported on a common stand D. One of the plates B is attached to the stand by means of a hinge C, so that, though represented upright, it may be placed horizontally, and be thus withdrawn from the vicinity of the plate A, the support of which is made of glass. On electrifying the insulated plate positively, the plate B, expressly placed close to A, is rendered — by induction; and, as happens in the Leyden jar, the excitement of B will be proportional to that of A. The — charge of B tends to preserve the + charge of A, which may consequently receive still more electricity by contact with any + surface, without losing what it had previously acquired. Thus is electricity accumulated or *condensed* on A; so that a substance too feebly excited to produce any appreciable effects of itself, may by repeated contact with the insulated plate of a condenser communicate a charge of considerable intensity. The effect of the accumulation is made apparent by withdrawing B, and bringing A in contact with a delicate electrometer. The condenser is much employed in experiments of delicacy, and the plate A is often permanently fixed on the gold leaf electrometer.

Fig. 1.



7. The *Electrophorus* is another contrivance of Volta's, which acts by induced electricity. It consists essentially of two parts; one being a flat cake of resin, made by pouring melted resin into a shallow plate or circular dish of tinned iron, and the other a disk of brass, of rather smaller diameter than the resin, supplied with a glass handle. The surface of the resin is negatively excited by friction or flapping with silk or flannel, and the brass disk is laid upon it. The resin being a non-conductor retains its own electricity in spite of the super-imposed brass, and decomposes the combined electricities of the latter, causing its under surface to be +, and its upper —. On touching the brass with the finger, its upper surface is neutralized; and on then withdrawing the brass plate, it is found to have an excess of + electricity. On replacing the brass as before, the resin, having lost none of its electricity in the process, acts again upon the metallic disk as on the first occasion, and will continue so to act for an indefinite number of

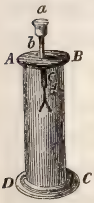
times. Kept in a dry place, the electrophorus will keep in action for months.

ELECTROSCOPES AND ELECTROMETERS.

It is very important, in experiments on electricity, to possess easy methods of discovering when a substance is electrified, of ascertaining its *intensity* or the degree to which it is excited, and distinguishing the kind of excitement. The means for effecting these objects are founded on electrical attraction and repulsion, and the instruments employed for the purpose are called *Electroscopes* and *Electrometers ;* the latter denoting the intensity of electricity,—the former merely indicating excitement, and the electrical state by which it is produced. The term electrometer, however, is often indiscriminately applied to all such instruments, since the methods of ascertaining the kind of excitement give at the same time some idea of its intensity.

Gold Leaf Electrometer.—Several simple electroscopic methods have already been indicated (page 72). Small balls made of the pith of elder are used for the same purpose. A single pith ball, suspended by a cotton thread, is attracted by a feeble electrified substance. Also, when two pith balls are suspended from the same point by cotton threads of equal length, and an electrified body is placed near them, the two balls are thrown by induction into the same electric state, and diverge. The gold leaf electrometer, figure 2, invented by Bennett, acts upon the same principle, but is far more delicate. It consists of a glass cylinder cemented below upon a brass plate CD, and covered above by a brass plate AB, pierced in its centre for the insertion of a glass tube *bc*, the top of which is closed by a brass plate *a* : into this plate is screwed a thick brass wire, which passes through the glass tube, and from the lower end *d* of which two slips of gold leaf are suspended. These different parts are put together while quite dry, all the joinings are secured by wax cement, and the glass is covered by lac varnish. The effect of these arrangements is to insulate the plate *a* with its wire and gold leaves, while the latter are secure against being moved by currents of air. The approach of any electrified body, even though feebly excited, to the plate *a*, is immediately detected by the divergence of the leaves, as shown in the figure. The instrument is equally useful in indicating the kind of excitement, provided the plate and leaves be permanently electrified, which may easily be done on the same principle as in charging the metallic disk of an electrophorus. If the plate be thus charged with + electricity, the leaves diverge, and continue divergent for some time if the air be

Fig. 2.



dry. In this state, the approach of a body charged with + electricity has a contrary effect.

Quadrant Electrometer.—An instrument much used for estimating the degree or intensity of electricity is the *quadrant electrometer*, invented by Henley. This instrument, though convenient for experiments of illustration, is not suited to those of research, wherein the object is to examine the effects of substances feebly electrified, and ascertain their relative forces with accuracy.

Torsion Electrometer.—This instrument, invented by Coulomb, is peculiarly fitted for scientific investigation. It consists of a small needle of gum-lac *c d*, fig. 3, suspended horizontally by a silk thread as spun by the silkworm, or by a fine silver wire *a b* ; on the point of the needle is fixed a small gilt ball made of the pith of elder ; and the whole is covered with a glass case to protect it from moisture and currents of air. The pith ball, when the apparatus is at rest, is in contact with the knob *e* of a metallic conductor *fe*, which passes through a hole in the glass case, and is secured in its place by cement ; but when an excited body is made to touch the conductor, the pith ball in contact with it is similarly excited, and recedes from it to an extent proportional to the degree of excitement. The needle consequently describes the arc of a circle, which is measured on the graduated arc AB, and in its revolution twists the supporting thread more or less according to the length of the arc described. The torsion thus occasioned calls into play the elasticity of the thread, —a feeble but constant force, which opposes the movement of the needle, measures by the extent to which it is overcome the repulsive force exerted, and brings back the needle to its original position as soon as the electric equilibrium is restored. It has been proved that the force which causes the torsion is exactly proportional to the arc described by the needle.

Fig. 3.

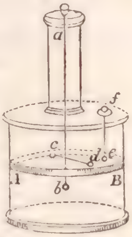
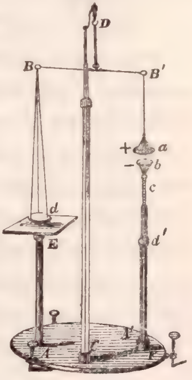


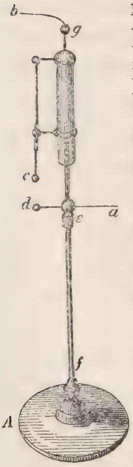
Fig. 4.



Balance Electrometer.—Harris has made a happy application of the common balance and weights to estimate the mutual attraction of oppositely electrified surfaces. The apparatus, figure 4, consists of a brass beam BB′, supported by a conductor CD standing on a wooden frame A A′ ; *d* is a scale for holding weights, and E its support ; *a*, *b*, are gilt cones made of light wood, *a* being suspended by a silver wire from B′, and *b* insulated by the glass support A′*d*′. The instrument is prepared for use by placing *a* and *d* in exact equipoise ; the cone *a* is suspended so that its base shall be opposite and parallel to the base of the cone *b*, as may be done by means of three adjusting screws in the frame A A′; and *b* is raised by help of a graduated brass slide *c*, until the bases of the cones are just in contact. The cone *b* is then depressed to any desired distance, which may be varied at will during an experiment, and it is connected with the inner coating of a Leyden jar, the outer coating of which communicates with the frame A A′, and along C D B′ with the cone *a*: these cones may thus be made parts of a charged Leyden jar, and be oppositely excited, as indicated by the signs + and —. The attractive forces exerted between their bases tend to draw down the cone *a* into contact with *b*, discharging the jar; but before it can do so, it has to overcome the weight which may be in the scale *d*. By this ingenious contrivance any number of attractive forces are estimated by a common standard, namely, the number of grains which each is able to raise.

Unit Jar.—This is another contrivance by Harris, and is a most important addition to our stock of electrical apparatus. It is formed of a small inverted Leyden jar, figure 5, supported and insulated by a slender glass rod *ef*, which is covered with lac varnish, and fixed into a wooden frame A. The inner coating of this jar is in metallic contact with a brass ball *d* and a wire *a*, which wire communicates with the prime conductor of an active electrical machine; whereas the brass ball *c* and wire *b* are connected with its outer coating. If the wire *b* be held in the hand, or otherwise communicate with the ground, the electrical machine being in action, the jar is charged in the usual manner, and is discharged by a spark passing between the two brass balls *c* and *d*. The interval may be increased or diminished by causing one of the balls to be moveable by means of a slide or screw. It will be readily conceived that successive sparks through the same interval must be caused by equal quantities of electricity; and experiment shows this to be the case, provided the apparatus is clean and dry, and the charges are taken nearly at the same time, that is, while the air in relation to temperature, pressure, and moisture, may be considered constant. On taking six successive sparks we employ six times as much electricity as for one charge, and three times as much as for two charges, the quantity of electricity being proportional to the number of charges. It is on this account Harris introduced the term unit jar. It is used for charging Leyden jars or batteries with known proportions of electricity.

Fig. 5.



Electric Intensity.—Before concluding this account of electrometers, it will be useful to refer to the kind of information which they supply. From their mode of action, it is plain that they indicate the *degree* of electric excitement, the remoteness from the unexcited state, a condition expressed by the terms *tension* and *intensity*. If two insulated brass disks of equal size be supplied with equal quantities of free electricity, they will affect an electrometer equally, and therefore their intensity or tension is equal ; but if one of the disks be larger than the other, the smaller will have the highest tension. In fact, one square inch of the smaller disk will possess more free electricity than the larger, and that is precisely the condition which constitutes differences of intensity. Of any number of electrified substances. that will have the highest intensity which has the most free electric fluid on unity of surface.

LAWS OF ELECTRICAL ACCUMULATION.

1. The quantity of free electricity which an insulated conductor is capable of receiving is independent of its quantity of matter. Thus, two brass spheres of the same size, one solid and the other hollow, will take equal quantities of electricity, and possess equal intensities. The cause of this is referrible to the second law.

2. The free electricity of an insulated conductor is always accumulated on its surface, where it forms a layer or stratum enveloping the substance on every side, and therefore possessed of the same figure. The cause of free electricity being disposed upon the surface of conductors is ascribed to the mutual repulsion of its particles, which gives them a tendency to recede as far as possible from each other, and to be arrested at the surface solely by some counteracting force, such as the interposition of an imperfect conductor.

3. The mode in which electricity is distributed over the surface of a conductor is dependent on its figure. On a sphere it forms an uniform stratum of equal thickness all around, that is, each part of the surface has the same quantity of electricity as any other part of equal size. But on an ellipsoid the stratum is thickest at the extremities of the longer axis, and the accumulation at those parts is greater and greater as the length of that axis becomes more and more predominant. In all conductors which are much longer than broad, as in a narrow metallic bar, as also in those which have elongated pointed terminations, the principal accumulation is at the ends and projecting points.*

The unequal accumulation of electricity on conductors is a direct consequence of the law of electric repulsion ; and Poisson, assuming the truth of that law, has arrived by calculation at the very same conclusions which Coulomb obtained by experiment. Those who are prepared to follow such very high mathematical inquiries are referred to Poisson's original Essay to the article on Electricity by Whewell in the Encyclopedia Metropolitana, and to a late work on Electricity by Murphy.

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* This has been established experimentally by Coulomb.

4. The electric fluid accumulated at the surface of conductors tends to escape by the repulsion of its particles. Its pressure against the air, or its effort to escape, at any part is considered proportional to the square of the quantity ; so that if the electric accumulations at four different parts of an excited conductor are as 1, 2, 3, and 4, the pressure against the air at those parts will be as 1, 4, 9, and 16. Hence electricity passes off with great rapidity from the ends or projecting points of conductors, a result quite conformable to experience. But the equilibrium of an excited conductor is perhaps never entirely restored by the direct diffusion of its excess due to its own repulsion ; for the conductor necessarily tends to induce a state opposite to itself in contiguous conductors and in the circumambient air, and then the attraction of oppositely electrified surfaces is called into play.

5. Coulomb proved experimentally, by aid of his torsion electrometer, that the repulsion of two similarly electrified bodies varies inversely as the square of their distances.

6. The attraction of two oppositely electrified bodies varies inversely as the square of the distance between them. Coulomb, who verified this law by experiment, also showed that the attractive force, the distance being constant, varies by the same law as that for repulsion just stated.

Harris has given a beautiful demonstration of these laws by means of his balance electrometer and unit jar, the cones *a*, *b*, of figure 4, being connected respectively with the outer and inner coatings of a large Leyden jar. On giving to it a constant charge by means of the unit jar, and varying the distance, the weights raised, or the attractive force, were found to vary inversely as the square of the distance between the cones. On preserving the distance constant, giving a charge capable of raising one grain, and then successively doubling, trebling, and quadrupling the quantity first given to the inner coating, the weights raised were 4, 9, and 16 grains.

7. It may be inferred from the law No. 6, that when, in two oppositely excited bodies, the whole quantity of electricity and the distance vary together and at the same rate, the attractive force will be unchanged. This has been fully proved by Harris. In fact,

doubling the electricity on both cones, is to quadruple the attractive force between them ; and doubling the distance diminishes the force by four times : the force is thus diminished by one cause as much as it is increased by the other, and therefore continues unchanged.

8. Harris ascertained the nature of the influence exerted by the atmosphere over the striking distance of a charged Leyden jar, that is, the interval through which the electricity will pass, so as to discharge it, by including the balls connected with its outer and inner coating within glass vessels susceptible of exhaustion. He then found that the resistance to the passage of a charge varies as the square of the density of the air. Agreeably to the same law, the striking distance, when the charge is constant, varies inversely as the density of the air: a charge which strikes through one inch of air when the barometer is at 30 inches, will pass through two inches in air so rarified as to support only 15 inches of mercury, and through four inches when the mercurial column is 7·5 inches. Hence in a perfect vacuum a Leyden jar ought to discharge itself through any interval ; and in the higher parts of the atmosphere, where the air is much rarified, two oppositely excited clouds will neutralize each other, though separated by very great distances.

It is not apparent from the preceding remarks, whether the striking distance is influenced by change of the density or the elasticity of the confined air, since in rarefying air by the air-pump, the rarefaction increases, and the elasticity decreases at the same rate. Harris has shown, contrary to what one might anticipate, that the influential condition is density, and not elasticity. For on rarefying air by heat so as to preserve its original elasticity, the striking distance was exactly the same as in cold air rarefied to the same degree by the air pump ; and in air first rarefied by the air pump, and then heated until it had recovered its original elasticity, its volume and density being kept the same, the varied elasticity had no influence on the charge required to pass through a constant distance. From these and similar experiments Harris infers that the remarkable conducting power known to be possessed by hot air is due to its rarity alone.—Though I have not had occasion to repeat these experiments on hot air, I have entire confidence in their accuracy ; inasmuch as, not to mention the known skill and exactness of Harris, I find that the striking distance for the same charge is greater in air than in carbonic acid gas, and greater in hydrogen gas than in air, the elasticities being equal.

9. The continuance of an excited charge on an insulated conductor is commonly ascribed to the pressure of the air. An opposite

opinion, however, has been maintained. Morgan (Phil. Trans. 1785) published some experiments to prove that a space entirely free from air, such as a Torricellian vacuum, is non-conductor of electricity: and Cavallo (Treatise on Electricity) showed that exhaustion may be carried very far within the bell-jar of an air pump without an electrified body placed under it losing its charge. On repeating these experiments, at the request of Harris, I obtained similar results. These phenomena appear to indicate the existence of an adhesive force between the particles of electricity and the surface of bodies, which causes an obstacle to their escape.

10. Some elegant and most ingenious experiments have been made by Wheatson to determine the velocity of electricity (Phil. Trans. 1834). His principal conclusions are the following :—

1. The velocity of electricity along a copper wire exceeds that of light through the planetary space.

2. The disturbance of the electric equilibrium in a wire communicating at its extremities with the two coatings of a charged jar, travels with equal velocity from the two ends of the wire, and occurs latest in the middle of the circuit.

3. The light of electricity of high tension has a less duration in passing as a spark than the millionth part of a second.

HISTORICAL NOTICE.

The science of electricity is of modern origin. The knowledge of the ancients was confined to the fact that amber and the *lyncurium* (supposed to be tourmaline) acquired the property of attracting light bodies by friction. It was not known that other bodies may be similarly excited until the commencement of the 17th century, when Gilbert of Colchester detected the same property in a variety of other substances, and thereby laid the foundation of the science of electricity. A few additional facts were noticed during the same century by Boyle, Otto de Guericke, and Wall, and in 1709 Hawkesbee published an account of many curious electrical experiments ; but no material progress was made until Stephen Grey (Phil. Trans. 1729 to 1733) drew the distinction between conductors and non-conductors of electricity, and illustrated it by new and striking experiments. Soon after, Dufay in France distinguished between the two kinds of electricity ; and in 1759 (Phil. Trans. li. 340.) Symmer added the important fact that friction developes both kinds of electricity at the same time, an observation which led to the theory of two electric fluids as now understood. These discoveries, added to the confirmation of Franklin's opinion as to the identity of the cause of lightning and electricity, fixed the attention of scientific men upon the new study, and soon acquired for it a high rank among the sciences.

For further details respecting its origin and early progress the reader may consult the history of electricity by Priestly.

SECTION IV.

GALVANISM.

The science of Galvanism owes its name and origin to the experiments on animal irritability made by Galvani, Professor of Anatomy at Bologna, in the year 1790. In the course of the investigation he discovered the fact, that muscular contractions are excited in the leg of a frog recently killed, when two metals, such as zinc and silver, one of which touches the crural nerve, and the other the muscles to which it is distributed, are brought into contact with one another. Galvani imagined that the phenomena are owing to electricity present in the muscles, and that the metals only serve the purpose of a conductor. He conceived that the animal electricity originates in the brain, is distributed to every part of the system, and resides particularly in the muscles. He was of opinion that the different parts of each muscular fibril are in opposite states of electrical excitement, like the two surfaces of a charged Leyden phial, and that contractions take place whenever the electric equilibrium is restored. This he supposed to be effected during life through the medium of the nerves, and to have been produced in his experiments by the intervention of metallic conductors.

The views of Galvani had several opponents, one of whom, the celebrated Volta, Professor of Natural Philosophy at Pavia, succeeded in pointing out their fallacy. Volta maintained that electric excitement is due solely to the metals, and that the muscular contractions are occasioned by the electricity thus developed passing along the nerves and muscles of the animal. To the experiments instituted by Volta we are indebted for the first voltaic apparatus, which has properly received the name of the *voltaic pile ;* and to the same distinguished philosopher belongs the real merit of laying the foundation of the science of Galvanism (Phil. Trans. 1800).

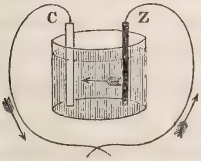
The identity of the agent concerned in the phenomena of galvanism and of the common electrical machine, is now a matter of demonstration. Voltaic and common electricity are due to the same force, excited by different conditions, operating in general in a different manner and under different circumstances. The effects of the latter are caused by a comparatively small quantity of electricity brought into a state of insulation, in which state it exerts a high intensity, as evinced by its remarkable attractive and repulsive energies, and by its power to force a passage through obstructing media. In galvanism the electric agent is more intimately associated with other substances, it is developed in large quantity, but never attains a high tension, and produces its peculiar effects while flowing along conductors in a continuous current.

VOLTAIC ARRANGEMENTS OR CIRCLES.

Arrangements for exciting galvanism are divided into simple and compound ; the former being voltaic circles in their most elementary form, and the latter a collection of simple circles acting together ; it will hence be proper to commence the description of them with the most simple.

Simple Voltaic Circles.—When a plate of zinc and a plate of copper are placed in a vessel of water, and the two metals are made to touch each other, either directly or by the intervention of a metallic wire, galvanism is excited. The action is, indeed, very feeble, and not to be detected by ordinary methods ; but if a little sulphuric acid be added to the water, numerous globules of hydrogen gas will be evolved at the surface of the copper. This phenomenon continues uninterruptedly while metallic contact between the plates continues, in which state the circuit is said to be *closed ;* but it ceases when the circuit is broken, that is, when metallic contact is interrupted. The hydrogen gas which arises from the copper plate results from water decomposed by the electric current, and its ceasing to appear indicates the moment when the current ceases. In this case the voltaic circle consists of zinc, copper, and interposed dilute acid ; and the circle gives rise to a current only when the two metals are in contact. This arrangement is shown in figure 1, where metallic contact is readily made or broken by means of copper wires soldered to the plates. By employing a galvanometer, it is found that a current of + electricity continually circulates in the closed circuit from the zinc through the liquid to the copper, and from the copper along the conducting wires to the zinc, as indicated by the arrows in the figure. A current of − electricity agreeably to the theory of two electric fluids, ought to traverse the apparatus in a

Fig. 1.



direction precisely reversed; but for the sake of simplicity I shall hereafter indicate the course of the + current only.

Two metals are not absolutely essential to the formation of a simple circle. A current is obtained from one metal and two liquids, provided the liquids are such that a stronger chemical action takes place on one side of the metal than on the other. Nay, a plate of metal, with two portions of the same liquid, but of different strength, forms a simple circle; and even the same liquid, of but one strength, if one side of the metal be more rapidly acted on by it than the other, will produce a current. This may be effected, for example, by having one side rough, the other polished.

An interesting kind of simple voltaic circle is afforded by commercial zinc. This metal, as sold in the shops, contains traces of tin and lead, with rather more than one per cent. of iron, which is mechanically diffused through its substance: on immersion in dilute sulphuric acid, these small particles of iron and the adjacent zinc form numerous voltaic circles, transmitting their currents through the acid which moistens them, and disengaging a large quantity of hydrogen gas. Pure distilled zinc is very slowly acted on by dilute sulphuric acid of sp. gr. ranging from 1·068 to 1·215; but if fused with about 2 per cent., or rather less, of iron filings, it is as readily dissolved as commercial zinc. Sturgeon has remarked that commercial zinc, with its surface amalgamated, which may be done by dipping a zinc plate into nitric acid diluted with two or three parts of water, and then rubbing it with mercury, resists the action of dilute acid fully as well as the purest zinc. This fact, of which Faraday in his late researches has made excellent use, appears due to the mercury bringing the surface of the zinc to a state of perfect uniformity, preventing those differences between one spot and another which are essential to the production of minute currents; one part has the same tendency to combine with electricity as another, and cannot act as a discharger to it (Faraday).

While the current formed by the contact of two metals gives increased effect to the affinity of one of them for some element of the solution, the ability of the other metal to undergo the same change is proportionally diminished. Thus, when plates of zinc and copper touch each other in dilute acid, the zinc oxidizes more, and the copper less, rapidly than without contact. This principle was beautifully exemplified by the attempt of Davy to preserve the copper sheathing of ships. A sheet of copper immersed in sea-water, or a solution of chloride of sodium, in an open vessel, undergoes rapid corrosion; and a green powder commonly termed sub-muriate of copper, but which is really an oxy-chloride, is generated: atmospheric oxygen dissolved in sea-water unites both with copper and sodium, the latter yields its chlorine to another portion of copper, and the oxide and chloride of copper unite. But if the copper be in contact with zinc or some metal more electro-positive than itself, the zinc undergoes the same change as the copper did, and the latter is preserved. Davy found that the quantity of zinc required thus to form an efficient voltaic circle with copper was very small. A piece of zinc as large as a pea, or the head of a small round nail, was found fully adequate to preserve 40 or 50 square inches of copper; and this wherever it was placed, whether at the top, bottom, or middle of the sheet of copper, or under whatever form it was used. And when the connection between different pieces of copper was completed by wires, or thin filaments of the 40th or 50th of an inch in diameter, the effect was the same; every side, every surface, every particle of the copper remained bright, whilst the iron or the zinc was slowly corroded. Sheets of copper defended by 1-40th to 1-1000th part of their surface of zinc, malleable and cast iron, were exposed during many weeks to the flow of the tide in Portsmouth harbour, and their weight ascertained before and after the experiment. When the metallic protector was from 1-40th to 1-150, there was no corrosion nor decay of the copper; with smaller quantities, such as 1-200th to 1-460th, the copper underwent a loss of weight which was greater in proportion as the protector was smaller; and as a proof of the universality of the principle, it was found that even 1-1000th part of cast iron saved a certain proportion of the copper (Phil. Trans. 1824).

Unhappily for the application of this principle in practice, it is found that unless a certain degree of corrosion takes place in the copper, its surface becomes foul from the adhesion of sea-weeds and shell-fish. The oxy-chloride of copper, formed when the sheathing is unprotected, is probably injurious to these plants and animals, and thus preserves the copper free from foreign bodies.

Simple voltaic circles may be formed of very various materials: but the combinations usually employed consist either of two perfect and one imperfect conductor of electricity, or of one perfect and two imperfect conductors. The substances included under the title of perfect conductors are metals and charcoal, and the imperfect conductors are water and aqueous solutions. It is essential to the operation of the first kind of circle, that the imperfect conductor act chemically on one of the metals: and in case of its attacking both, the action must be greater on one metal than on the other. It is also found generally, if not universally, that the metal most oxidized is positive with respect to the other, or bears to it the same relation as zinc to copper in figure 1. Davy, in his Bakerian lecture for 1826 (Phil. Trans.), to which the reader is referred, has given lists of different arrangements of both the kinds just mentioned.

Faraday has shown that the presence of water is not essential. A battery may be composed of other liquid compounds, such as a fused metallic chloride, iodide, or fluoride, provided it is decomposable by galvanism, and acts chemically on one metal of the circle more powerfully than on the other.

Metallic bodies are not essential to the production of galvanic phenomena. Combinations have been made with layers of charcoal and plumbago, of slices of muscle and brain, and beet-root and wood; but the force of these circles, though accumulated by the union of numerous pairs, is extremely feeble, and they are very rarely employed in practice.

Of the simple voltaic circles described by Davy, the only one used for ordinary purposes is that composed of a pair of zinc and copper plates excited by an acid solution arranged as in figure 1. The form and size of the apparatus are exceedingly various. Instead of actually immersing the plates in the solution, a piece of moistened cloth may be placed between them. Sometimes the copper plate is made into a cup for containing the liquid, and the zinc is fixed between its two sides, as shown by the accompanying transverse vertical section, figure 2; care being taken to avoid actual contact between the plates, by interposing pieces of wood, cork, or other imperfect conductor of electricity. Another contrivance, which is much more convenient, because the zinc may be removed at will and have its surface cleaned, is that represented by the annexed woodcut (fig. 3). C is a cup made with two cylinders of sheet copper of unequal size, placed one within the other, and soldered together at bottom, so as to leave an intermediate space *a a a*, for containing the zinc cylinder z and the acid solution. The small copper cups *b b* are useful appendages; for by filling them with mercury, and inserting the ends of a wire, the voltaic circuit may be closed or broken with ease and expedition. This apparatus is very serviceable in experiments on electro-magnetism.

Fig. 2.

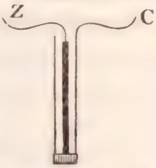
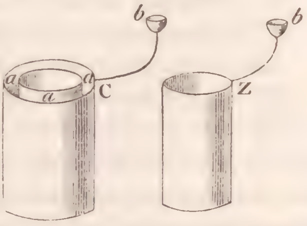
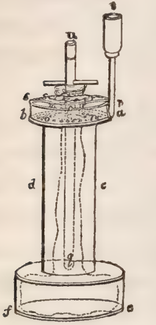


Fig. 3.



Another kind of circle may be formed by coiling a sheet of zinc and copper round each other, so that each surface of the zinc may be opposed to one of copper, and separated from it by a small interval. The London Institution possesses a very large apparatus of this sort, made under the direction of Pepys, each plate of which is 60 feet long and two wide. The plates are prevented from coming into actual contact by interposed ropes of horsehair; and the coil, when used, is lifted by ropes and pulleys, and let down into a tub containing dilute acid. The contrivance of opposing one large connected surface of zinc to a similar surface of copper originated with Hare of Philadelphia, who, from its surprising power of igniting metals, gave it the name of *calorimotor*.

Fig. 4.



An excellent arrangement has been described by Daniell, of which fig. 4 represents a modification more simple and perhaps equally effective. It consists of a cylinder of copper, *a b c d e f*, 3 inches wide from *a* to *b*, 1½ inches from *c* to *d*, and four inches from *e* to *f*, the corresponding heights being half an inch, 5 inches, and 2 inches; *l m n o*, is a collar of copper, which by the arms *r r*, *s s*, rests on the top of the cylinder, and to which a membranous tube formed of the gullet of an ox is tied, the membrane being longer than the copper cylinder, so as to be baggy below and nearly fill the space *e f*; *u p q*, is a rod of amalgamated zinc resting on the collar *l m n o*, by means of a piece of wood *r s*, which perforates it; *u t*, are cups to hold mercury for making contact. Between the membrane and copper cylinder is poured a saturated solution of blue vitriol, and within the membrane dilute sulphuric acid of about sp. gr. 1·136, which is made with 1 measure of strong acid and 8 of water. The exciting acid is thus in contact with the zinc, but not with the copper. When this circle is in action, the electric current passes from the zinc through the acid, membrane, and solution of blue vitriol to the copper. The arrangement is founded on two important principles, established by Daniell:—

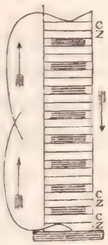
1. However active a circle, as made heretofore, may be when first excited, its energy is known rapidly to diminish, and in a few minutes to fall much below its original power. Daniell has traced the cause to reduction of oxide of zinc by nascent hydrogen at the surface of the copper plate, whereby this metal becomes coated with zinc, and is thus more or less converted at its surface into a zinc plate; and as two zinc plates under like conditions do not produce a current, of course the action declines. In the new circle this defect is avoided by the membranous septum which protects the copper plate from contact with the solution of zinc: the nascent hydrogen reduces oxide of copper, and a film of bright copper is deposited on the copper plate, thus constantly presenting a clean good conducting surface; while the hydrogen itself, not escaping as gas, no longer opposes an obstacle, as

it does when allowed to assume the gaseous form, to the passage of electricity, from the solution to the copper plate. To supply the loss of oxide of copper, a copper disc, *a v x b*, studded with holes like a cullender, is supplied, on which rest crystals of blue vitriol, whereby the solution is kept saturated, and its conducting power preserved. When the acid within the membrane is exhausted, the membrane itself is removed, and fresh acid supplied ; but to prevent the necessity of frequent renewal, the lower part of the membrane is made to act as a reservoir of acid.

2. The zinc of a pair of plates may be much reduced in size without any loss of power: strong chemical action on a small surface of zinc, a good conducting solution, and a bright large surface of copper, are conditions by which a powerful action is ensured. This is indicated by Davy's protectors for copper sheathing (page 89); but it was not previously known that the principle was applicable to the construction of voltaic apparatus. The great merit of this circle is its *constancy:* by keeping up the supply of blue vitriol and acid, its energy will continue invariable for hours, or for an indefinite period. A similar apparatus has been described by Mullins (Phil. Mag. & An. ix. 122).

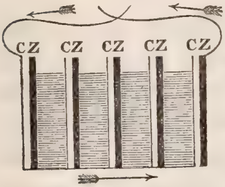
Compound voltaic circles.—This expression is applied to voltaic arrangements which consist of a series of simple circles. The first combinations of the kind were described by Volta, and are now well known under the names of *voltaic pile* and *crown of cups.* The voltaic pile is made by placing pairs of zinc and copper, or zinc and silver plates, one above the other, as in figure 5, each pair being separated from those adjoining by pieces of cloth, rather smaller than the plates, and moistened with a saturated solution of salt. The relative position of the metals in each pair must be the same in the whole series; that is, if the zinc be placed below the copper in the first pair, the same order should be observed in all the others. Without such precaution the apparatus would give rise to opposite currents, which would neutralize each other more or less according to their relative forces. The pile, which may consist of any convenient number of combinations, should be contained in a frame formed of glass pillars, fixed into a piece of thick dry wood, by which it is both supported and insulated. Any number of these piles may be made to act in concert by establishing metallic communication between the × extremity of each pile and the — extremity of the pile immediately following.

Fig. 5.



The voltaic pile is now rarely employed, because we possess other modes of forming galvanic combinations which are far more powerful and convenient. The galvanic battery proposed by Cruickshank consists of a trough of baked wood, about 30 inches long, in which are placed at equal distances 50 pairs of zinc and copper plates previously soldered together, and so arranged that the same metal shall always be on the same side. Each pair is fixed in a groove cut in the sides and bottom of the box, the points of junction being made water-tight by cement. The apparatus thus constructed is always ready for use, and is brought into action by filling the cells left between the pairs of plates with some convenient solution which serves the same purpose as the moistened cloth in the pile of Volta. By means of the accompanying woodcut the mode in which the plates are arranged will be easily understood.

Fig. 6.



Other modes of combination are now in use, which facilitate the employment of the voltaic apparatus and increase its energy. Most of these may be regarded as modifications of the crown of cups. In this apparatus the exciting soltuion is contained in separate cups or glasses, disposed circularly or in a line ; each glass contains a pair of plates ; and each zinc plate is attached to the copper of the next pair by a metallic wire, as represented in figure 7. Instead of glasses, it is more convenient in practice to employ a trough of baked wood or glazed earthenware, divided into separate cells by partitions of the same material ; and in order that the plates may be immersed into and taken out of the liquid conveniently and at the same moment, they are all attached to a bar of dry wood, the necessary connection between the zinc of one cell and the copper of the adjoining one being accomplished, as in figure 8, by a slip or wire of copper.

Fig. 7.

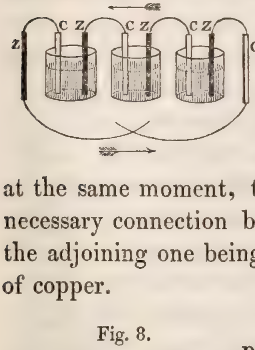
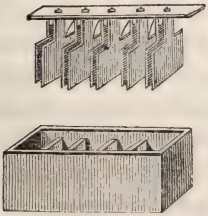


Fig. 8.



A material improvement in the foregoing apparatus was suggested by Wollaston (Children's Essay in Phil. Trans. 1815), who recommended that each cell should contain one zinc and two copper plates, so that both surfaces of the former metal might be opposed to one of the latter. The plates communicate with each other, and the zinc between them with the copper of the adjoining cell. An increase of one half the power is said to be obtained by this method.

The size and number of the plates may be varied at pleasure. It is now recognized, however, that increasing the number of plates beyond a very moderate limit gives for most purposes no proportionate increase of power; so that a battery of 50 or 100 pair of plates, thrown into vigorous action, will be just as effective as one of far greater extent.

A very effective battery, from its constancy of action, convenience, cheapness, and power, is made with Daniell's simple circles (page 92). Twenty of these, arranged on a wooden tray in two rows, has an energy sufficient for the performance of most experiments of demonstration or research.

Another most efficient battery is that of Smee, which is formed of plates of amalgamated zinc and of platinised silver; that is, silver, the surface of which is covered with platinum deposited on the metal in a pulverulent form. This battery is excited by dilute sulphuric acid, and, although not strictly a constant battery, yet continues in vigorous and nearly equal action for a very considerable period. Ten pairs of plates, 4 or 6 inches square, are sufficient for most of the ordinary experiments, decomposing water with great energy. One pair answers very well indeed for electro-magnetic experiments, and for the electrotype. The reader is referred to Mr. Smee's work for details.

Another excellent battery is that devised by Bunsen, in which cylinders of zinc are placed within hollow cylinders of prepared charcoal, and excited by nitric acid. Six or eight pairs of very moderate size exert an amazing power of developing heat and light, as in experiments of deflagration. This battery is described in the Annalen der Chemie und Pharmacie.

It must be remembered that in a compound circle, the extreme plates at either end, not being in contact with the exciting fluid, are in reality superfluous, and serve only as conductors. Hence the current, instead of flowing from the zinc to the copper, seems to flow from the copper to the zinc. But if we extract the extreme plates, which serve only as conductors, it is then seen that the direction of the current corresponds to that of the simple circle (see fig. 6).

During the action of a simple circle, as of zinc and copper, excited by dilute sulphuric acid, all the hydrogen developed in the voltaic process is evolved at the surface of the copper. This fact is not apparent when common zinc plates are used, owing to the numerous currents which form on the surface of the zinc (page 89); but when a plate of amalgamated zinc and another of platinum are introduced into dilute sulphuric acid of sp. gr. 1·068, no gas whatever appears until contact between the plates is made, and then hydrogen gas rises solely from the platinum, while zinc is tranquilly dissolved. On weighing the amalgamated plate before and after the action has continued for half an hour or an hour, and collecting the hydrogen gas evolved during that interval, the weight of the hydrogen set free and of zinc dissolved will be as 1 to 32·3, being the ratio of their chemical equivalents. Faraday, who has proved this, has also shown that in a compound voltaic circle, say of 10 amalgamated zinc plates and 10 of platinum, each of the former during a given period of action loses exactly the same weight, and from each of the latter an equivalent quantity of hydrogen gas is evolved. This separation of one ingredient of the exciting solution at one plate, while the element previously combined with it unites with the other plate, seems essential to voltaic action. It is in some way connected with the passage of the current across the exciting liquid. Oxygen in a free state may by oxidizing zinc cause electric excitement; but the voltaic current is not established unless the oxygen formed part of a previous liquid compound in contact or communication with both the plates.

Among the different kinds of voltaic apparatus is usually placed the electric column of De Luc, which is formed of successive pairs of silver and zinc, or silver and Dutch-metal leaf, separated by pieces of paper, arranged as in a voltaic pile. It is remarkable for its power of exhibiting attractions and repulsions like common electricity, but cannot produce chemical decomposition or any of the effects most characteristic of a voltaic current, and is rather an electrical than a voltaic instrument. It is quoted as a proof of electric developement by contact, since it will continue in action for years without being cleaned or taken to pieces. True it is that the more oxidable metal of the column is slowly corroded, and that no electricity is excited when the paper is quite or nearly free from hygrometric moisture, the presence of which is necessary to the oxidation of the zinc and copper; but at the same time the quantity of electricity excited seems so disproportioned to the corrosion, that the one can scarcely be assigned as the cause of the other.

LAWS OF THE ACTION OF VOLTAIC CIRCLES.

Electricians distinguish between *quantity* and *intensity* in galvanism, as in ordinary electricity; and by most persons, as also in this work, the same meaning is attached to them. The electric intensity of a voltaic circle is most correctly estimated by the divergence which in the broken circuit it causes in a gold leaf or other electrometer; and as the intensity is never considerable, it is often necessary to employ a condenser. The charges accumulated on the extreme plates of a voltaic circle cannot acquire a high tension, because the liquid which separates them is a good conductor for all charges except such as are of very feeble intensity. Accordingly, a simple circle has necessarily a very feeble tension. The circle which gives the highest tension is one which excites electricity sufficent for duly charging the apparatus, while it opposes an obstacle to spontaneous discharge. A battery of numerous small plates excited by water, or a weak saline or acid solution, fulfils these conditions.

The quantity of electricity circulating in a voltaic battery is exactly the same in all its parts. It is found to be exactly proportional to the magnetic and chemical effects which it is capable of producing; and hence the quantity of electricity moving through any closed circuit is readily estimated either by the deflection which it causes on a magnetic needle, or by its power of chemical decomposition. When quantity of electricity is alone desired, a single pair of plates is just as useful as a compound circle.

The following numerical results were obtained by Ritchie, by means of a magnetic galvanometer.

1. The power of a single pair of plates in deflecting the magnetic needle is directly proportional to the surface of the plates which is covered with dilute acid.

2. A plate of zinc introduced into a rectangular cup of copper, as in figure 2, page 91, deflects the needle twice as much as when one side of the zinc and the adjacent surface of copper are protected by a coating of cement from the action of the acid solution.

3. The deflection produced by a pair of plates, in an acid solution of uniform strength, varies inversely as the square root of the distance between them,—a law previously established by Cumming.

4. The same law, as previously deduced by Cumming and Barlow, applies to variations in the length of the wire by which the zinc and copper plates are connected. If, all other circumstances being uniform, the conducting wire varies from 4 feet to 1 foot in length, the deflecting power will vary in the ratio of 1 to 2. Ritchie has stated that with short metallic wires the deflection varies inversely as the square root of the length of the whole circuit, that is, of the solid and liquid conductors taken together.

Ritchie has also shown, agreeably to general observation, that the deflecting power of a compound circle is not increased by increasing the number of its plates. This is another proof that the direct influence of a number of plates is to increase the intensity and not the quantity of electricity; for the prevailing opinion that the magnetic needle takes no cognizance of intensity is fully borne out by the experiments of Faraday.

Though the quantity of a compound decomposed by a battery is proportional to the actual quantity of electricity which passes, yet, as a compound exposed to voltaic action is almost always an imperfect conductor, the quantity of electricity capable of passing through it varies with its intensity. Hence chemical decomposition depends on quantity and intensity together, and affords a criterion of the increased tension of a compound circle due to an increase in the number of its plates.

EFFECTS OF GALVANISM.

The effects produceable by voltaic combinations are conveniently divisible into the electrical, magnetic, and chemical phenomena.

I. *Electrical Effects.*—These are so called, as being analagous to the effects of ordinary electricity. An active broken circuit produces the phenomena of electric repulsion, as already stated. A Leyden phial may also be charged by contact of its inner coating with one wire of the circle, while the outer communicates either with the other wire or with the ground: a full charge, though of feeble intensity, is almost instantly given. On approximating the wires of an active circle, a brilliant spark passes between them just before contact, as well as in the act of breaking contact. When the electric current is made to pass through the body of an animal, as on holding the conducting wires in the hands, previously moistened to facilitate conduction, a distinct shock is felt, which is powerful when a battery of high tension is employed. On sending the current through fine metallic wires or slender pieces of plumbago or compact charcoal, these conductors become intensely heated, the wires even of the most refractory metals are fused, and a vivid white light appears at the charcoal points, equal, if not superior, in splendour to that of phosphorous burning in oxygen gas; a phenomenon in no wise referrible to combustion, as it takes place in a vacuum or under water. If the electric current pass through thin metallic leaves, the metals burn with vivid scintillations:—gold leaf emits a white light tinged with blue, silver a beautiful emerald green light, copper a blueish white light with red sparks, lead a rich purple, and zinc a brilliant white light fringed with red. In burning leaves, fusing wire, and igniting charcoal, a large quantity of electricity is the only requisite:

the large battery of Children, though capable of fusing several feet of platinum wire, had an electric tension so feeble, that it did not affect the gold leaves of the electrometer, gave a shock scarcely perceptible even when the hands were moist, communicated no sensible charge to a Leyden jar, and could not produce chemical decomposition. If the quantity and intensity of the current are both great, an arc of light appears between the charcoal points after contact, even through an interval of an inch or more.

The electrical effects of galvanism are so similar to those of the electrical machine, that it is impossible to witness and compare both series of phenomena without referring them to the same agent. The question of identity early occupied the attention of Wollaston, who made some very beautiful and conclusive experiments to prove that not only are the electrical effects of the machine produceable by galvanism, but that the chemical effects of galvanism may be characteristically produced by a current from the electrical machine (Phil. Trans. 1801). The subject has been examined anew by Faraday, who has subjected the effects of electricity and galvanism to a minute and critical comparison: he has obtained ample proof of the decomposing power of an electric current from an electrical machine, both by repeating the experiments of Wollaston and devising new ones of his own. He has also completed the chain of evidence by deflecting a magnetic needle with an electric current from the machine; an observation, indeed, which had been previously made by Colladon. These researches have led to a remarkable contrast between the quantity of electricity concerned in the production of voltaic and ordinary electrical phenomena. Faraday states that the quantity of electric fluid employed in decomposing a single grain of water is equal to that of a very powerful flash of lightning; and this statement, surprising as it is, is supported by such strong evidence, that it is difficult to withhold assent to the assertion.

II. *Magnetic Effects of Galvanism.*—The power of lightning in destroying and reversing the poles of a magnet, and in communicating magnetic properties to pieces of iron which did not previously possess them, was noticed at an early period of the science of electricity, and led to the supposition that similar effects may be produced by the common electrical and voltaic apparatus. Attempts were accordingly made to communicate the magnetic virtue by means of electricity and galvanism; but no results of importance were obtained till the winter of 1819, when Oersted of Copenhagen made his famous discovery, which forms the basis of a new branch of science. (An. Phil. xvi. 273.)

The fact observed by Oersted was, that the metallic wire of a closed voltaic circle,—and the same is true of charcoal, saline fluids, and any conducting medium which forms part of a closed circle,—causes a magnetic needle placed near it to deviate from its natural position, and assume a new one, the direction of which depends upon the relative position of the magnet and the wire. On placing the wire above the needle and parallel to it, the pole next the negative end of the battery always moves westward; and when the wire is placed under the needle, the same pole goes towards the east. If the wire is on the same horizontal plane with the needle, no declination whatever takes place; but the magnet shows a disposition to move in a vertical direction, the pole next the negative side of the battery being depressed when the wire is to the west of it, and elevated when it is placed on the east side.

When the influence of the earth's magnetism on the needle which impedes its free motion is counteracted by another magnet placed near it, the needle places itself directly across the connecting wire; so that the real tendency of a magnet is to stand at right angles to an electric current.

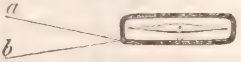
The communicating wire is also capable of attracting and repelling the poles of a magnet. When the connecting wire is held vertically near a horizontally suspended magnet, on the west side of it, and approached to the north pole, attraction ensues, till they come very close, when repulsion follows. When the wire is approached to the south pole, similar effects ensue, in an inverted order. If the wire be held on the east side, the effects are reversed; the current in both cases being supposed to flow upwards through the wire.

The discovery of Oersted was no sooner announced, than the experiments were repeated and varied by philosophers in all parts of Europe, and, as was to be expected, new facts were speedily brought to light. Among the most successful of those who early distinguished themselves were Ampère, Biot, and Arago, of Paris, and Davy and Faraday in this country. A host of other able men have since added their contributions; and their joint labours have established an altogether new science, *Electro-Dynamics*, which has already become one of the most important branches of physical knowledge, and still offers a rich harvest of discovery to its cultivators. Those who wish to enter deeply into the study of this subject should consult the *Recueil d'Observations Electro-Dynamiques* by Ampère, Cumming's Manual of Electro-Dynamics, Murphy's Treatise on Electricity, and the second edition of Barlow's Essay on Magnetic Attractions. A less mathematical, and therefore more generally intelligible, treatise has been drawn up with great ability by Roget, and published as part of the Library of Useful Knowledge; and a Popular Sketch of Electro-Magnetism has been given by Watkins of Charing-cross. To these works I refer as supplying that detail of the facts and theories of electro-dynamics, which, as belonging more to the province of physics than chemistry, is unsuited to the design of this volume.

The phenomena of electro-dynamics are solely produced by electricity in motion. The passage of electricity through solid or liquid conductors is essential; in fact, a magnetic needle is a *galvanoscope*, by which means the existence and direction of an electric current may be detected. In this way, Ampère demonstrated the fact, that electricity passes uninterruptedly through the battery when the circuit is closed, and not at all in the broken circuit.

But a magnetic needle will not only indicate the existence and direction of an electric current: it may even serve, by the degree of deflection, as an exact measure of its force. When used for this purpose, under the name of *galvanometer*, some peculiar arrangements are required in order to ensure the requisite delicacy and precision. Experiment proves that a magnet is equally affected by every point of a conductor along which an electric current is passing; so that a wire transmitting the same current will act with more or less energy, according as the number of its parts contiguous to the needle is made to vary. On this principle is constructed the *Galvanometer* or *Multiplier* of Schweigger. A copper wire is bent into a rectangular form consisting of several coils, and in the centre of the rectangle is placed a delicately suspended needle, as shown in figure 9. Each coil adds its influence to that of the others; and as the current, in its progress along the wire, passes repeatedly above and below the needle in opposite directions, their joint action is the same. In order to prevent the electricity from passing laterally from one coil to another in contact with it, the wire should be covered with silk. The ends of the wire, *a* and *b*, are left free for the purpose of communication with the opposite ends of the voltaic circle. The needle ought to be rendered *astatic*, that is, the influence of the earth's magnetism ought to be destroyed by placing another magnet above the rectangle, having its north pole adjacent to the south pole of the first. The instrument is thus rendered extremely delicate.

Fig. 9.

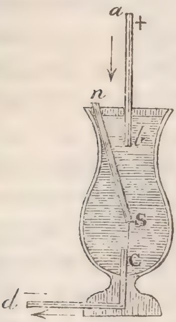


The mutual influence of a magnetic pole and a conducting wire changes with the distance between them; and experiment leads to the conclusion that the attraction of a magnetic pole on a *single* point of a conductor varies as the square of the distance; the same well known law which regulates the distribution of heat and light, as well as electricity.

On examination, all the phenomena described by Oersted are found to be referrible to a force acting tangentially on the poles of a magnet, and in a plane perpendicular to the direction of the current.

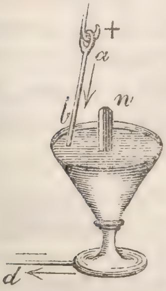
The same principle accounts for the rotation of a magnetic pole round a current, discovered by Farady. Into the centre of the bottom of a cup, as in the vertical section, figure 10, a copper wire c *d* was inserted, a cylindrical magnet *n* s was attached by a thread to the copper wire c, and the cup was nearly filled with mercury, so that pole *n* only of the magnet projected. A conductor *a b* was then fixed in the mercury perpendicularly over the wire c. On connecting the conducting wires with the opposite ends of a battery, a current was transmitted from one wire through the mercury to the other. If the + current descend, the north pole of the magnet, if uppermost, will rotate round the wire *a b*, passing from east through the south to west like the movements in the hands of a watch; and if the current ascend, the line of rotation will be reversed. Under similar circumstances the south pole would in each case rotate in the opposite direction.

Fig. 10.



If a magnetic pole rotate round a conductor, a conductor will be equally disposed to rotate round a magnetic pole, just as a magnet moves towards iron or iron towards a magnet, according as one or other is free to move. Accordingly, on fixing a magnet vertically in the middle of a cup of mercury, fig. 11, and transmitting a current by the movable conductor *a b* through the mercury, and along a second conductor *d*, fixed as before in the bottom of the cup, Faraday found that the free extremity *b* of the wire moved round the pole of the magnet in a direction similar to the last.

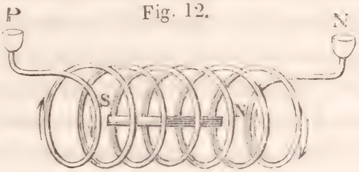
Fig. 11.



It is obvious that the direction of rotation imparted by a fixed current to the moveable pole, will be identical with that which the same pole tends to impart to the same current.

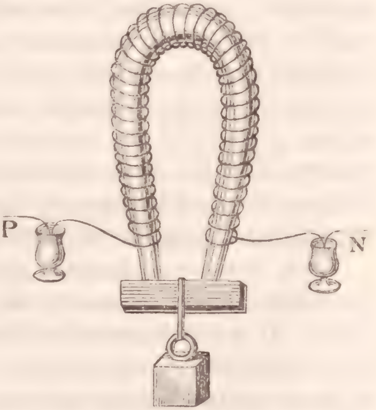
A current of voltaic electricity not only determines the position of a magnet, but renders steel permanently magnetic. This was observed nearly at the same time by Arago and Davy, who found that when needles are placed at right angles to the conducting wire, permanent magnetism is communicated; and Davy also succeeded in producing this effect even with a shock of electricity from a Leyden phial. Arago, at the suggestion of Ampère, made a voltaic conductor into the form of a helix, in the axis of which he placed a needle, as in figure 12. As in this arrangement the current nearly in every part of its course is at right angles to the needle, and as each coil adds its effect to that of the others, the united action of the helix is extremely powerful. The needle was thus fully magnetized in an instant.

Fig. 12.



Though soft iron does not retain magnetism, its magnetic properties while under the influence of an electric current are very surprising. A piece of soft iron, about a foot long and an inch in diameter, is bent into the form of a horse-shoe, a copper wire is twisted round the bar at right angles to its axis, and an armature of soft iron, to which a weight may be attached, is fitted to its extremities, as in figure 13. On connecting the ends of the wire with a simple voltaic circle, even of small size, the soft iron instantly becomes a powerful magnet, and will support considerable weights. Increasing the number of coils gives a great increase of power; but as the length of wire required for that purpose diminishes the influence of the current the following arrangement has been successfully adopted. The total length of copper wire intended to be used is cut into several portions, each of which, covered with silk or cotton thread to prevent lateral communication, is coiled separately on the iron. The ends of all the wires are then collected into two separate parcels, and are made to communicate with the same voltaic battery, taking care that the + current shall pass along each wire in the same direction. The current is thus divided into a number of branches, and has only a short passage from one end of the battery to the other, though it gives energy to a multitude of coils. A combination of this kind, connected with a battery of five feet square, supported 2063 pounds, or nearly a ton weight.

Fig. 13.



In witnessing the influence of voltaic conductors over the directive property of magnets, and in inducing magnetism, it is difficult to divest one's self of the conviction that these conductors, while transmitting a current, are themselves magnetic. This belief was early entertained by those who repeated the experiments of Oersted, and experimental evidence of its truth was speedily adduced. Arago and Davy found that a copper wire connecting the end of a voltaic combination attracted iron filings, but that they instantly fell off as soon as the circuit was broken; and a conductor, when its movements were not impeded by friction or gravity, was proved by Ampère to be obedient, like an ordinary magnet, to the magnetic agency of the earth.

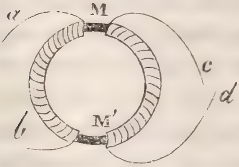
Since, therefore, the conductors just described may be regarded as magnets, such magnetized conductors ought mutually to repel or attract each other, when poles of the same or a different nature are adjacent; and as the action of a whole spiral or rectangle is merely the accumulated effect of its individual parts, it is fair to presume that each small portion of a conductor has its opposite sides in a state of opposite polarity, and that two such contiguous portions should attract or repel each other on the same principle as the spirals of which they constitute a part. Nay, even different parts of the same conductor ought to be mutually attractive or repulsive. These inferences from the facts already detailed were fully demonstrated by Ampère soon after the discovery of Oersted. He proved that two voltaic conductors, or two portions of the same conductor, attract each other when the currents have the same direction, and are mutually repulsive when they are traversed by opposite currents; which is exactly what would be anticipated from the magnetic influence of conductors.

These are a few examples of the numerous facts experimentally proved by Ampère concerning the action of voltaic conductors on each other. It is to this branch of the subject the term of *Electro-Dynamics*, or the science of electricity in motion, is sometimes restricted, while the mutual action of conductors and magnets is called *Electro-Magnetism;* but these two branches are so entirely parts of the same science, that I have included both under Ampère's term of Electro-Dynamics. Any one who has studied the few preceding pages with moderate care, cannot fail to trace a close analogy between a helix traversed by an electric current and a magnet. The former is affected by other voltaic conductors, by the poles of a magnet, and by the magnetism of the earth, in the same manner as the latter. It was this similarity, or rather identity, of action which led Ampère to his theory of magnetism. He supposes that the polarity of every magnet is solely owing to the circulation, within its substance and at its surface, of electric currents, which continually pass around all its particles in planes perpendicular to its axis. On placing a magnet in its natural position of north and south, the direction of its currents is as follows; they descend on the east side, passing under the magnet from east to west and ascending on the side next the west. In like manner are currents supposed to circulate within the earth, especially near its surface, passing from east to west in planes parallel to the magnetic equator. These terrestrial currents cause all bodies which are freely suspended, and are possessed of electric currents, to place themselves in such a position that the current on their under side should flow in parallelism, and in the same direction, with that in the earth immediately beneath. That the existence of such currents will account for the directive property of the earth, follows from the mutual action of conductors: and Barlow, to render the analogy still more complete, constructed a hollow sphere of wood in which electric currents were made to circulate in the same direction as they are thought to do in the earth; and by placing an astatic needle on different parts of its surface, he found that all the phenemena of terrestrial magnetism might be imitated. Observation has even supplied a cause for the existence of currents in the earth, moving in the direction which theory requires. The diurnal rotation of our planet on its axis exposes its surface to be heated in a direction passing from east to west; and the discoveries which have been made in thermo-electricity sufficiently prove the probability of electric currents being established in the conducting matter of the earth by the successive heating of its parts. In short, the theory of Ampère connects the facts of electro-dynamics with the phenomena of terrestrial magnetism, and affords a splendid instance of the application of mathematical analysis to physical research.

Volta electric Induction.—The developement of electricity by the vicinity of an excited body, already described under the name of induced electricity led Faraday to inquire whether electricity in motion, as well as that of tension and at rest, may not be excited by induction. Though baffled in his early attempts, he at last succeeded in laying open a new branch of electro-dynamics, which vies in interest and importance with the fundamental discovery of Oersted (Phil. Trans. 1831). A copper wire 203 feet long was passed in form of a helix round a large block of wood, and an equal length of a similar wire was wound on the same block and in the same direction, so that the coils of each helix should be interposed, but without contact, between the coils of the other. The ends of one of the helices were connected with a galvanometer, and the other with a strong galvanic battery, with the view of ascertaining whether the passage of an electric current through one helix would induce a current in the adjoining helix. It was found that the galvanometer needle indicated a current at the moment both of completing and breaking the circuit, but that in the interval no deflection took place; and similarly the induced currents readily magnetized a sewing needle, while the electric current along the inducing helix was in the act of beginning or ceasing to flow, but at no other period. In the former case the direction of the induced current is opposite to that of the inducing current, and in the latter case it is the same. This phenomenon is distinguished by Faraday under the name of *volta-electric induction.*

The inducing power of a magnet greatly exceeds that of an electric current. A ring of soft iron was covered to nearly half its extent by several helices, the ends of which were brought together so as to constitute a compound helix terminating in the conductors, *a b*, figure 14; and on the other half of the ring were arranged similar helices which communicated by *c d* with a galvanometer. The two sets of helices were thus separated from each other by portions of the ring M M′, and were protected by cloth from direct contact with the ring itself. At the moment the wires *a b* touched the ends of a voltaic combination, the galvanometer was strongly affected: the needle then returned to its former position, and remained there until the voltaic circuit was broken, when the needle was again deflected as strongly as before, but in the opposite direction. The action was still greater when both compound helices were on the same part of the ring, the induction being increased apparently by the closer contiguity of the helices. Other arrangements have been devised by Faraday, for producing similar results; and to the action in all these cases he has given the name of Magneto-electric induction.

Fig. 14.



The phenomena arising from magneto-electric and volta-electric induction are manifestly owing to the same condition of the induced wire: the action on the needle, though different in force, is identical in kind. It is equally clear that the agent brought into operation in the induced wire is an electric current, or, to dismiss the language of theory, that the induced wire is in the same electric state as the conducting wire in a closed voltaic circle. Its power in magnetizing steel and deflecting a magnet is sufficient evidence of this; but Faraday, by magneto-electric induction, succeeded in throwing a frog's leg into spasms by connecting it with the induced wire, and by arming the ends of that wire with points of charcoal, and separating them at the instant the galvanic circuit of the inducing wire was broken or restored, sparks of electricity were obtained. The mode in which soft iron contributes to the effect is likewise obvious. An electric current circulating round a bar of soft iron has been shown to convert it into a temporary magnet possessed of surprising power (page 103); and it is doubtless to this magnet, called into temporary existence by the electric current, most of the induced electricity is to be ascribed. Faraday reduced this to certainty by surrounding a cylinder of soft iron with one helix connected with the galvanometer, and converting the soft iron into a temporary magnet, not by a voltaic battery, but by placing at each end of the cylinder the opposite pole of a magnet. During the act of applying the magnetic poles to the iron, the galvanometer needle was deflected; and the deflection was reproduced, but in the opposite direction, when the magnetism of the iron was ceasing by the removal of the magnet. Similarly, when a helix was wound on a hollow cylinder of pasteboard, and a real magnet was introduced, the galvanometer was deflected: the needle then remained quiescent so long as the magnet was left in the cylinder; but in the act of its removal, the needle was again deflected, though, as usual, in the opposite direction.

These singular phenomena, which establish such new and intimate relations between voltaic and magnetic action, and supply additional evidence in favour of Ampère's beautiful theory of magnetism, have led to an experiment by which, at first view, an electric spark appeared to be derived from the magnet itself. After Faraday had announced his experiment, above mentioned, of obtaining a spark from the induced wire, other attempts were made to affect the same object with a magnet, without the aid of galvanism. The first person who succeeded in this country was Forbes, who operated with a powerful loadstone (Phil. Trans. ed. 1832). A helix of copper wire was formed round the middle of a cylinder of soft iron, which was of such length that its extremities reached from one pole of the loadstone to the other. On applying and withdrawing the soft iron cylinder to and from the poles of the loadstone, magnetism was alternately created and destroyed within it. At these periods of transition, electric currents were induced in the helix surrounding the soft iron; and when, at these instants, metallic contact between the conducting wires of the helix was broken, an electric spark was visible. Forbes succeeded best by connecting one wire with a cup of mercury, and removing the other wire from contact with its surface at the instant when an assistant withdrew the armature of soft iron from the loadstone. In this experiment, therefore, the electricity was obtained from the helix, and was induced in it by the soft iron while in the act of acquiring or losing magnetism. The same experiment was performed by Faraday with a loadstone belonging to Daniell ; and shortly before the experiment of Forbes, Nobili and Antinori succeeded with an ordinary steel magnet. Pixii in Paris afterwards performed this experiment with great effect by causing a strong horse-shoe magnet to revolve upon an axis, its poles passing in rapid succession in front of a soft iron armature of the same form ; and a still better arrangement is to cause the armature to revolve in front of the poles of a powerful magnet, as in the instrument fitted up by Saxton, and exhibited at the Adelaide-rooms, London. It produces brilliant sparks, renders platinum wire red hot, and gives a strong shock. It explodes gunpowder, and also a mixture of oxygen and hydrogen gases, and decomposes water rapidly.

Intimately associated with magneto-electric induction, if not referrible to the very same origin, is the induction of electric currents by movement. On introducing a magnet into a hollow helix of copper wire, or other solid conductor, as also on withdrawing the magnet after its introduction, an electric current was momentarily induced in the wire ; and if, the magnet being stationary, the helix were moved in its vicinity, an electric current is likewise induced. The direction of the movement is not immaterial : it is essential that the plane in which the conductor moves should form an angle with the axis of the magnet; and the most powerful currents were induced, when the plane of motion was at right angles to that axis, and hence parallel to the electric currents which Ampère supposes to exist in the magnet. With regard to the direction of an induced current, Faraday's researches establish this law, deduced by Ritchie : if a wire conducting voltaic electricity produce on magnets or conductors certain motions, whether repulsive, attractive, or rotatory, and if the battery be removed, the ends of the wires brought into metallic contact, and the same motions be produced by mechanical means, the conductor will have the same electric state induced in it as it had when connected with the battery. (Phil. Mag. 3rd series, iv. 12.)

Faraday has applied this principle in a most happy manner to explain the phenomena of rotation discovered by Arago. If a plate of copper be revolved close to a magnetic needle suspended so that it may rotate in a plane parallel to the plate, the needle will rotate in the same direction ; and, reciprocally, a rotating magnet tends to give rotation to a contiguous copper-plate. The same effects are produced by the rotation not only of all metals, but, according to Arago, of all bodies whether solid, liquid, or gaseous. These effects, which Faraday has principally examined in reference to the rotation of metals, are entirely owing to electric currents induced by the rotation, and flowing at right angles to the direction of motion.

If motion in the vicinity of a magnet induce an electric current, the same effect would be anticipated from the magnetic influence of the earth ; and this fact has been proved by Faraday by most decisive and interesting experiments. When a bar of soft iron is held in the position of the dipping needle, the direction of which, in regard to terrestrial magnetism, is analogous to the axis of a common magnet, it acquires magnetic properties ; and accordingly, on introducing a soft iron cylinder into a hollow helix of copper placed in the line of the dip, a galvanometer connected with the helix was instantly affected. But the use of iron may be dispensed with altogether ; for when a helix of copper wire was simply moved at right angles to the dipping needle, electric currents were induced by the magnetism of the earth. The form of a helix is not even necessary : the movement of a piece of copper wire across the line of dip developed currents in the wire. The same effect was produced by the rotation of a copper plate placed horizontally so as to be nearly at right angles to the line of dip ; and the revolution of a copper globe acted in the same manner. Faraday concludes that the rotation of the earth on its axis ought similarly to influence the conducting matters of its surface ; and that electric currents should be thereby induced from the equatorial regions to either pole. He throws out the suggestion whether the aurora borealis and australis may not be produced by the returning currents passing from the holes of the earth into the atmosphere.

It may here be mentioned, although our space only permits us to allude to the subject, that Faraday, pursuing his profound researches, has very recently shewn that all bodies possess a certain relation to magnetism ; and that while such substances as the loadstone and a few others, which are *magnetic*, point, when freely suspended, towards the magnetic poles of the earth, or in other words place themselves in the magnetic meridian, all other substances, when freely suspended, and in favourable circumstances, place themselves in a position at right angles to the magnetic meridian. These latter Faraday calls *diamagnetic* bodies.

The reader is referred to the last series of researches by Faraday, (Phil. Mag. 1846), and his attention is also directed to the recent experiments of Baron Reichenbach,* altogether independent of those of Faraday, which tend to prove that light, visible only to certain sensitive persons, is emitted from the poles of powerful magnets, and is even capable of acting on the prepared plate of the Daguerreotype.

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* See an Abstract of Baron Reichenbach's Researches in Magnetism, by the Editor of this work. There are many phenomena observed by Baron Reichenbach, which appear to be connected with those described by Faraday. In a letter to the Editor, dated 15th of June, 1846, Baron Reichenbach states that he has obtained the fullest confirmation of his previous observations, from experiments made on persons in perfect health, of whom he had already examined fifteen ; and that he no longer employs individuals in a morbid condition for his experiments. —W. G.

III. *Chemical Effects of Galvanism.*—The chemical agency of the voltaic apparatus, to which chemists are indebted for a most powerful instrument of analysis, was discovered by Carlisle and Nicholson, soon after the invention was made known in this country. The substance first decomposed by it was water. When two gold or platinum wires are connected with the opposite ends of a battery, and their free extremities are plunged into the same cup of water, but without touching each other, hydrogen gas is disengaged at the — and oxygen at the + wire. By collecting the gases in separate tubes as they escape, they are found to be quite pure, and in the exact ratio of two measures of hydrogen to one of oxygen. When wires of a more oxidable metal are employed, the result is somewhat different. The hydrogen gas appears as usual at the — wire; but the oxygen, instead of escaping, combines with the metal, and converts it into an oxide.

This important discovery led many able experimenters to make similar trials. Other compound bodies, such as acids and salts, were exposed to the action of galvanism, and all of them were decomposed without exception, one of their elements appearing at one side of the battery, and the other at its opposite extremity. An exact uniformity in the circumstances attending the decomposition was also remarked. Thus, in decomposing water or other compounds, the same kind of body was always disengaged at the same side of the battery. The metals, inflammable substances in general, the alkalies, earths, and the oxides of the common metals, were found at the — wire; while oxygen, chlorine, and the acids, went over to the + surface.

In performing some of these experiments, Davy observed, that if the conducting wires were plunged into separate vessels of water, made to communicate by some moist fibres of cotton or amianthus, the two gases were still disengaged in their usual order, the hydrogen in one vessel, and the oxygen in the other, just as if the wires had been immersed into the same portion of that liquid. This singular fact, and another of the like kind observed by Hisinger and Berzelius, induced him to operate in the same way with other compounds, and thus gave rise to his celebrated researches on the transfer of chemical substances from one vessel to another (Phil. Trans. 1807). In these experiments two agate cups, N and P, were employed, the first communicating with the —, the second with the + wire of the battery, and connected together by moistened amianthus. On putting a solution of sulphate of potassa or soda into N, and distilled water into

P, the acid very soon passed over to the latter, while the liquid in the former, which was at first neutral, became distinctly alkaline. The process was reversed by placing the saline solution in P, and the distilled water in N, when the alkali went over to the — cup, leaving free acid in the other. That the acid in the first experiment, and the alkaline base in the second, actually passed along the amianthus, was obvious; for on one occasion, when nitrate of oxide of silver was substituted for the sulphate of potassa, the amianthus leading to N was coated with a film of metal. A similar transfer was effected by putting distilled water into N and P, and a saline solution in a third cup placed between the two others, and connected with each by moistened amianthus. In a short time the acid of the salt appeared in P, and the alkali in N. It was in pursuing these researches that Davy made his great discovery of the decomposition of the alkalies and earths, which till then had been regarded as elementary. (Phil. Trans. 1808.)

Such is a statement of the principal phenomena of electro-chemical decomposition according to the earlier experiments. The facts then observed were received as established truths of science, and passed current without suspicion or scrutiny till the present time. But Faraday, in his revision of this part of the science, has not only added much new matter, but proved that several conclusions, which were considered as fundamental maxims, are erroneous. Before describing his results, however, I will define the new terms which he has had occasion to introduce.—In order to decompose a compound, it is necessary that it should be liquid, and that an electric current should pass through it; an object easily affected by dipping into the liquid the ends of the metallic wires which communicate with the voltaic circle. These extremities of the wires are commonly termed *poles*, from a notion of their exerting attractive and repulsive energies towards the elements of the decomposing liquid, just as the poles of a magnet act towards iron; and each is further distinguished by the term *positive* or *negative*, according as it affects an electrometer with + or — electricity. Now Faraday contends that these poles have not any attractive or repulsive energy, and act simply as a path or door to the current: he hence calls them *electrodes*, ηλεκτϱον, and ὁδος, a way. The electrodes are the surfaces, whether of air, water, metal, or any other substance, which serve to convey an electric current into and from the liquid to be decomposed. The surfaces of this liquid which are in immediate contact with the electrodes, and where the elements make their appearance, are termed *anode* and *cathode*, from ανα, *upwards*, and ὁδος, the way in which the sun rises, and κατα, *down-*

wards, the way in which the sun sets. The anode is where the + current is supposed to enter, and the cathode where it quits, the decomposing liquid, its direction, when the electrodes are placed east and west, corresponding with that of the + current which is thought to circulate on the surface of the earth (page 105). To *electrolyze* a compound, is to decompose it by the direct action of galvanism, its name being formed from ηλεκτρον and λυω, *to unloose or set free;* and an electrolyte is a compound which may be electrolyzed. The elements of an electrolyte are called ions, from ιον, going, neuter participle of the verb to go. *Anions* are the ions which appear at the anode, and are usually termed the electro-negative ingredients of a compound, such as oxygen, chlorine, and acids; and the electro-positive substances, hydrogen, metals, alkalies, which appear at the cathode, are *cations.* Whatever may be thought of the necessity for some of these terms, the words electrode, electrolyze, and electrolyte, are peculiarly appropriate, and are already in use.

The principal facts determined by Faraday may be arranged under the following propositions:—

1. All compounds, contrary to what has been hitherto supposed, are not electrolytes, that is, are not directly decomposable by an electric current. But in making this assertion it is necessary to distinguish between primary and secondary decomposition. Water is an electrolyte, its hydrogen being delivered up at the – and its oxygen at the + electrode. A solution of hydrochloric acid is likewise an electrolyte, being resolved into chlorine and hydrogen. But nitric and sulphuric acids and ammonia are not electrolytes, though the first and last are decomposed by secondary action. Thus, on subjecting nitric acid to voltaic action, the water of the solution is electrolyzed, and its hydrogen arriving at the + electrode, decomposes the nitric acid, water being there reproduced and nitrous acid formed. So, in a solution of ammonia, the oxygen of decomposed water unites at the + electrode with the hydrogen of the ammonia, and nitrogen gas is evolved. Very numerous secondary actions are occasioned in this way, because the disunited elements are presented in a nascent form, which is peculiarly favourable to chemical action; and in many instances the electrode itself, which is commonly metallic, is chemically attacked. Thus, when chlorine is evolved against an electrode of gold, oxygen at one of some easily oxidable metal, as copper or iron, or sulphur against a silver electrode, chloride of gold, oxide of copper or iron, and sulphuret of silver, are generated. If these changes are caused by very feeble currents acting slowly as for weeks, months, or years, the new products have oppor-

tunity to assume regularly crystalline forms. It is by such means that Becquerel has succeeded in procuring artificial minerals exactly resembling those which are found in mines (Traité d'Electricité); and Crosse has since obtained similar results (Phil. Mag. and An. ix. 229). Taking these facts in conjunction with the researches of Fox on the electrical state of mineral veins, there can be no longer a doubt that feeble electric currents within fissures of rocks, induced by terrestrial magnetism, by variations of temperature at different parts of the rock, or by the different nature of the walls of the fissures, or of the solutions with which they are filled, may have been one principal source of metalliferous deposits; nor is it at all unreasonable or unphilosophical to suppose that the enormous mineral masses which now constitute our metalliferous veins may have been the work of such feeble currents acting during hundreds or thousands of centuries. Feeble agencies operative for a long period are often just as efficacious in effecting great changes as powerful agents at work during a short period; and Becquerel, in opening this new line of inquiry, has supplied a principle by which the scientific geologist may explain many of those obscure phenomena which fall within his observation.

2. Most of the salts which have been examined are resolvable into acid and oxide, apparently without reference to their proportions. But in compounds of two elements, the ratio of combination has an influence which has hitherto been wholly overlooked. No two elements appear capable of forming more than one electrolyte. Hydrochloric acid and fused metallic protochlorides, such as the chlorides of lead and silver, and protochloride of tin, are readily decomposed; while bichloride of tin and other perchlorides resist decomposition. Substances which consist of a single equivalent of one element and two or more equivalents of some other element, are not electrolytes: this is the reason why sulphuric and nitric acid and ammonia do not yield primarily to voltaic action. This principle bids fair to become very important in determining which of several compounds of two elements contains single equivalents. Water, which is remarkable for its easy decomposition, may hence be inferred to be a true binary compound.

3. It has been ascertained that most of the elements are *ions*, and it is probable that all of them are so; but there are several important elements, such as nitrogen, carbon, phosphorus, boron, silicon, and aluminium, which have not yet been proved to be *ions*. This arises from the difficulty of obtaining these elements in compounds fitted for electrolytic action.

4. A single *ion*, that is, one ion not in combination with another, has no tendency to pass to either of the electrodes, and is quite indif-

ferent to the passing current, unless it be itself a compound ion, and therefore electrolyzable. The character of true electrolytic action consists in the separation of *ions*, one passing to one electrode and another to the opposite electrode, and appearing there at the same instant, unless the appearance of one or both be prevented by some secondary action.

5. There is no such thing as a transfer of *ions* in the sense usually understood. In order that the elements of decomposed water should appear at the opposite electrodes, there must be water between the electrodes ; and for the similar separation of sulphuric acid and soda, there must be a line of particles of sulphate of soda extending from one electrode to the other. Thus, if a solution of sulphate of magnesia be covered with pure water, care being taken to avoid all admixture of particles, and the + metallic termination or pole touch the magnesian solution only, while the – pole is in contact with the water only, a deposit of magnesia occurs just where the pure water and the magnesian solution meet, and none reaches the – pole. In Davy's experiment, where sulphuric acid and soda appeared to quit each other, and pass over separately into a vessel of pure water, there was certainly by capillary attraction an actual transfer of the salt before decomposition occurred.

6. In the foregoing experiment a surface of water acts as the – electrode, clearly showing the contact of a metallic conductor with the decomposing liquid not to be essential. Faraday has proved that even air may serve as an electrode. A current from the prime conductor of an electrical machine was made to pass from a needle's point through air to a pointed piece of litmus paper moistened with sulphate of soda, and then to issue from a similarly moistened point of turmeric paper. True electrolytic action took place, the litmus becoming red and the turmeric paper brown, though both extremities of the decomposing solution communicated solely with a stratum of air.

7. Electro-chemical decomposition cannot occur unless an electric current is actually transmitted through the electrolyte ; or, in other terms, an electrolyte is always a conductor of electricity. Water, which conducts an electric current, ceases to do so when it passes into ice, and then also resists decomposition—an observation equally true of all electrolytes on becoming solid. Moreover, liquids which resist electro-chemical decomposition do not permit the current of a voltaic circle to pass. The alliance between conduction and decomposition is so constant, that the latter may be regarded as a means by which voltaic currents are transmitted through liquid compounds. Agreeably to this notion, solidity may interfere with conduction by chaining down the elements of a compound, and thereby preventing their

transfer to the electrodes. Improving the conduction of a liquid, as by adding sulphuric acid to pure water, increases the decomposing power of a voltaic circle, the exciting fluid within the apparatus remaining the same; and Faraday has proved that the quantity of a compound decomposed is exactly proportional to the quantity of electricity which passes, however much other circumstances, such as the size of electrodes and conducting wires, number and size of plates, and nature of exciting fluid, may vary. Changes in these conditions do, indeed, influence the quantity of electricity transmitted; but then the degree of chemical decomposition varies in the same proportion. The foregoing facts at first led to the opinion that the current of a voltaic circle cannot pass through liquids, except those of a metallic nature, unless decomposition ensues at the same time; but Faraday has noticed that when the intensity is too feeble to effect decomposition, a small quantity of electricity may be transmitted, sufficient to be discovered by a galvanometer. This does not, however, essentially interfere with the law just announced.

8. Chemical compounds differ in the electrical force required for decomposition. A current of very feeble tension suffices to decompose iodide of potassium, while a much higher intensity is required for disuniting the elements of water. The order of easy decomposition in the annexed substances is as follows:—Solution of iodide of potassium; fused chloride of silver; fused protochloride of tin; fused chloride of lead; fused iodide of lead; solution of hydrochloric acid; and water acidulated with sulphuric acid. By extending tables of this kind, a ready method will be known for comparing the tension of voltaic circles.

9. The conduction of the electric currents within the cells of a voltaic circle depends on chemical decomposition equally with that between platinum electrodes. No substance not an electrolyte can serve to excite a voltaic apparatus; and for the passage of electricity from plate to plate through the intervening solution, the separation of substances previously combined in the required ratio is essential. Neither free oxygen nor a solution of chlorine can excite a current, though they attack the zinc and develope electricity; and in a voltaic circle excited by dilute sulphuric acid, the electricity set in motion is due to decomposed water and oxidized zinc, and not at all to the union of the oxide of zinc with sulphuric acid. The platinum electrodes and intervening liquid may be viewed as one of the cells of the circle, except that the plates act merely as conductors, without any oxidation, the current passing in virtue of the decomposed solution. In the zinc and copper cells, the current is urged on

by the appetency of the zinc and oxygen to unite; whereas, in passing between the electrodes, the electricity has to surmount the mutual attraction of oxygen and hydrogen, or some similar force, without the assistance of any opposing affinity. Hence, in experiments on decomposition, the course of the electricity should be facilitated by employing large electrodes and wires, and placing them at a short distance from each other in a good conducting solution.

The principles above established show the importance of exciting all the cells of a voltaic circle with a liquid of the same strength. The electricity circulating in a voltaic apparatus with the conducting wires in contact, is equal to that which the feeblest cell is able to transmit, any chemical action in other cells more than sufficient for exciting that quantity being wasted.

THEORIES OF GALVANISM AND ELECTRO-CHEMICAL THEORY.

Of the theories proposed to account for the developement of electricity in voltaic combinations, three in particular have attracted the notice of philosophers. The first originated with Volta, who conceived that electricity is set in motion, and the supply kept up, solely by contact or communication between the metals (page 87). He regarded the interposed solutions merely as conductors, by means of which the electricity developed by each pair of plates is conveyed from one part of the apparatus to the other. Thus, in the pile or ordinary battery, represented by the following series:—

$$+ \quad \overbrace{\text{zinc copper}}^{3} \quad \overset{\longrightarrow}{\text{fluid}} \quad \overbrace{\text{zinc copper}}^{2} \quad \overset{\longrightarrow}{\text{fluid}} \quad \overbrace{\text{zinc copper}}^{1} \quad -$$

Volta considered that contact between the metals occasions the zinc in each pair to be +, and the corresponding copper plate to be —; that the + zinc in each pair except the last, being separated by an intervening stratum of liquid from the — copper of the following pair, yields to it its excess of electricity; and that in this way each zinc plate communicates, not only the electricity developed by its own contact with copper, but also that which it had received from the pair of plates immediately before it. Thus, in the three pairs of plates contained in brackets, the second pair was thought to receive electricity from the first only, and the third pair from the first and second. In batteries constructed on the principle of the crown of cups (fig. 6), the *electro-motion*, as Volta called it, is ascribed to metallic communication between the zinc of one glass and the copper of the adjoining one.

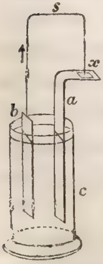
The second is the *chemical theory*, proposed by Wollaston. Volta attached little importance to the chemical changes which never fail to occur in every voltaic circle, whether simple or compound, considering them as casual or unessential phenomena, and therefore neglected them in the construction of his theory. The constancy of their occurrence, however, soon attracted notice. In the earlier discussions on the cause of spasmodic movements in the frog (page 87), Fabroni contended, in opposition to Volta, that the effect was not owing to electricity at all, but to the stimulus of the metallic oxide formed or of the heat evolved during its production. More extended researches soon proved the fallacy of this doctrine ; but Fabroni made a most ingenious use of the facts within his knowledge, and paved the way to the chemical theory of Wollaston.

Wollaston, fully admitting electricity as the voltaic agent, assigned chemical action as the cause by which it is excited. The repetition and extension of Volta's experiments by the English chemists speedily detected the error he had committed in overlooking the chemical phenomena which occur within the pile. It was observed that no sensible effects are produced by a combination of conductors which do not act chemically on each other; that the action of the pile is always accompanied by the oxidation of the zinc ; and that the energy of the pile in general is proportional to the activity with which its plates are corroded. Observations of this nature induced Wollaston to conclude that the process begins with the oxidation of the zinc,—that oxidation, or, in other terms, chemical action, was the primary cause of the developement of electricity,—that the fluid of the circle served both to oxidize the zinc and to conduct the electricity which was excited,—and that contact between the plates served only to conduct electricity, and thereby complete the circuit.

The third theory of the pile was proposed by Davy, and is intermediate between the two former. He adduced many experiments in support of Volta's statement, that the electric equilibrium is disturbed by the contact of different substances, without any chemical action taking place between them. He acknowledged, however, with Wollaston, that the chemical changes contribute to the general result ; and he maintained that, though not the primary movers of the electric current, they are essential to the continued and energetic action of every voltaic circle. The electric excitement was begun, he thought, by metallic contact, and maintained by chemical action.

The progress of inquiry since these theories first came into notice has gradually given more and more support to the views of Wollaston, and has at last, I apprehend, established it to the entire exclusion of the theory of Volta. The very fundamental position, that electricity is excitable as a primary result by the contact of different substances, is warmly contested, and, as some think, with strong reason, has been disproved (page 76); but admitting, for the sake of argument, that a *small* effect, which is all that can now be contended for, may thus be produced, it is altogether insignificant when contrasted with the astonishing phenomena exhibited by a voltaic circle. The experiments of De la Rive, in reference to this question, appear irreconcilable with the theory of Volta (An. de Ch. et Ph. xxxviii. 225; lxi. 38; lxii. 147). This ingenious philosopher contends that the direction of a voltaic current is not determined by metallic contact, nor even by the nature of the metals relatively to each other, but by their chemical relation to the exciting liquid. As the result of his inquiries, he states, that of two metals composing a voltaic circle, that one which is most energetically oxidized will be + with respect to the other. Thus, when tin and copper are placed in acid solutions, the former, which is most rapidly corroded, gives a + current through the liquid to the copper, as the zinc does in the circle in fig. 1; but, if they are put into a solution of ammonia, which acts most on the copper, the direction of the current will be reversed. Copper is + in relation to lead in strong nitric acid, which oxidizes the former most freely: whereas in dilute nitric acid, by which the lead is most rapidly dissolved, the lead is +. Even two plates of copper immersed in solutions of the same acid, but of different strengths, will form a voltaic circle, the plate on which chemical action is most free causing a current of + electricity to the other: nay, it is possible to construct a compound circle solely with zinc plates and one acid solution (page 89), provided the same side of each plate be more rapidly oxidized than the other.

Fig. 15.



The admirable researches of Faraday (Phil. Trans. 1833 & 34) supply conclusive evidence against the theory of Volta, proving metallic contact not to be essential to voltaic action, inasmuch as it is procured characteristically without contact. A plate of zinc, *a*, fig. 15, about 8 inches long by ½ an inch wide, was cleaned and bent at a right angle; and a plate of platinum, of the same width and 3 inches long, was soldered to a platinum wire *b s x*, the point of which, *x*, rested on a piece of bibulous paper lying upon the zinc, and moistened with a solution of iodide of potassium. On introducing the plates into a vessel, *c*, filled with dilute sulphuric and nitric acid, a + current instantly ensued in the direction of the arrow, as testified by the hydrogen evolved at the plate *a*, by the decomposed iodide of potassium, and by a galvanometer. We have thus a simple circle of the same construction and action as in figure 1, except in the absence of metallic contact.

Another proof, aptly cited by Faraday, of electric excitement, being independent of contact, is afforded by the spark which appears when the wires of a pair of plates in vigorous action are brought into contact. The spark is occasioned by the passage of electricity across a thin stratum of air; and therefore its production proves that electromotion really occurred while the wires were yet separated by a thin stratum of air, which permitted the electric current to pass, and anterior to their actual contact.

The arrangement of figure 15, however, though good for establishing a principle, is not adapted for ordinary practice. The moist paper at *x* is a much less perfect conductor than a metal, and thus obstructs the passage of the current; nay, it does more, for it tends to establish an opposite current. In fact, on removing the dilute acid from *c*, and putting the zinc plate, *a*, in contact with the plate of platinum, an ordinary simple circle would be formed, in which a positive current would flow from the zinc at *x* through the solution to and along the wire *x s b*. This current in Faraday's experiment was so feeble compared with the one excited by the acid solution, that its influence was scarcely appreciable; but if the opposed currents had been of the same force, no action would have ensued.

To explain how chemical action excites electricity, recourse is had to the electro-chemical theory, first started by Davy in his essay on Some Chemical Agencies of Electricity (Phil. Trans. 1807). The views of Davy, which in some form or other have been adopted by most persons who have speculated on this subject, are founded on the assumption, now rendered so much more plausible than in his day, that electrical and chemical attractions are owing to one and the same agent. He considered chemical substances to be endowed with *natural electric energies*; meaning thereby, that a certain electric condition, either + or −, is natural to the atoms or combining molecules of bodies; that chemical union is the result of electrical attraction taking place between oppositely excited atoms, just as masses of matter when oppositely excited are mutually attracted; and that ordinary chemical decomposition arises from two combined atoms being drawn asunder by the electric energies of other atoms more potent than those by which they were united. Electro-chemical decomposition was at once explained by Davy on the same principles. He regarded the metallic terminations or *poles* of a voltaic circle (page 111) as two centres of electrical power, each acting repulsively to particles in the same electric state as istelf, and by attraction on those which were oppositely excited. The necessary result was, that if the electric energy of the battery exceeded that by which the elements of any compound subject to its action were held together, decomposition followed, and each element was tranferred bodily to the pole by which it was attracted, passing through solutions not containing the original compound, and refusing to unite with substances for which under other circumstances it would have combined. Substances which appear at the + pole, such as oxygen, chlorine, and acids, were termed *electro-negative* substances; and those *electro-positive* bodies, which were separated at the — pole.

The views of Davy, both in his original essay and his subsequent explanations (Phil. Trans. 1826), were so generally and obscurely expressed, that chemists have never fully agreed, as to some points of the doctrine, about his real meaning. If he meant that a particle of free oxygen or free chlorine is in a negatively excited state, then his opinion is contrary to the fact, that neither of those gases affect an electrometer with — or any kind of electricity, any more than hydrogen gas or potassium alone exhibit any evidence of + excitement. If sulphur unites with oxygen because it has a + electric energy, why should it unite with potassium, which confessedly is far more + than itself? The only mode in which such facts as these seem reconcilable with the electro chemical theory is, to suppose all bodies in their uncombined state to be electrically indifferent, but that they have a natural appetency to assume one state in preference to another. Electro-negative bodies are such as assume negative excitement under a certain approximation to others which at the same time become positively excited, chemical union being the consequence. On this supposition, it is intelligible that sulphur may be + in relation to oxygen, and — to potassium, just as black silk is positively electrified by friction with sealing-wax, and negatively by white silk. Accordingly, Berzelius, and others who have since speculated on this subject, have been obliged to modify the theory as first given by Davy; and it is viewed at present in different ways by different persons. The following is what appears to me most correctly to harmonise with the laws of electricity and the phenomena to be explained:—A particle of zinc and a particle of oxygen, each possessed of + and — electricity, assume in combining opposite electric conditions, and combine in consequence of such assumption, the particles adhering together by virtue of their opposite states, just as two oppositely excited pith balls are mutually attractive. The zinc particle in becoming + gives off — electricity to the mass of zinc or other body to which it had belonged; and, in like manner, the particle of oxygen, in becoming —, supplies + electricity to adjacent particles of oxygen or other adjacent substances. Thus electro-positive bodies in the act of combining give off — electricity, and electro-negatives set free + electricity. In general, these opposite electricities instantly neutralize each other; but under favourable circumstances such effect is prevented. Thus in an experiment by De la Rive, of transmitting dry chlorine gas mixed with air through an insulated copper tube, chloride of copper is generated; if the gases pass onward in a continuous current, the + electricity set free by the chlorine is carried off by the air, while the tube is rendered negative by the — electricity lost by those particles of copper which combine with the chlorine.

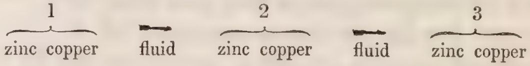
Chemical decomposition also excites electricity; and by this theory it ought to do so. For a particle of zinc in quitting oxygen is +, must recover — electricity before it can resume its natural state, and in doing so leaves contiguous substances +; and, similarly, the — oxygen renders objects — by robbing them of their + electricity. Hence, a body in combining excites in others an electric state opposite to that which it assumes; while in the act of decomposition it produces an effect exactly the reverse.

Again it follows from the theory, that unless the zinc can assume the + state by getting rid of — electricity, it cannot unite with oxygen; and that chemical union will more readily ensue, the more freely a conducting medium for carrying off such — electricity is supplied. This is applicable to Davy's method of preserving copper in sea-water (page 90). A piece of zinc in contact with copper corrodes rapidly by the copper carrying off its — electricity; while the copper thus constantly rendered —, is prevented from assuming the + state, and hence loses its power of uniting either with oxygen or chlorine. These principles readily apply to a simple voltaic arrangement, composed of zinc, copper, and dilute acid. In the broken circuit, the oxidation of the zinc causes the liquid, which supplies the oxygen, to be +; while the zinc plate is made — by the electricity given off by the oxidizing particle of zinc. This happens whether the copper plate is present or not. The + electricity diffused in the acid solution is in part taken up by the copper plate which thereby becomes +, and is in part lost by neutralizing the — electricity on the zinc plate. In the closed circuit, the — electricity on the zinc escapes along the conducting wire to the copper plate; the effect of which is to promote the oxidation of the zinc on the principle above stated, and by rendering the copper

—, to facilitate the extraction of + electricity from the liquid. A current of + electricity thus circulates from the zinc through the liquid to the copper, and of — electricity in the opposite direction (page 88). That plate which by chemical action with the liquid excites electricity, is called the *generating plate;* while the other is the *conducting plate,* because it performs the office of a conductor merely: in the common circle, zinc is the generating, and copper the conducting plate.

In a compound circle, represented by three pairs of plates, as in fig. 16, each pair of plates, indicated by the brackets, sends a current of + electricity from the zinc through the liquid to the copper, rendering each copper plate +, while each zinc plate is —. The first copper and second zinc plates, being oppositely electrified, neutralize each other; and the same occurs with the second copper and third zinc, as with any number of plates similarly situated. The extreme plates alone can evince an electric state, the zinc in the broken circuit being —, and the copper +; and if these plates are connected by a wire, they, like the other zinc and copper plates of the series, neutralize each other, and a continuous current is established through the whole battery, of + electricity in one direction, as shown by the arrows, and of — in the other. Thus, the quantity of electricity which circulates in one part of the closed battery, which is aptly called a *circle,* is, contrary to the notion of Volta (page 116), the same in every part (page 96). The influence of a number of plates is to augment the intensity only (page 94). This subject has been ably discussed by De la Rive. (An. de Ch. et Ph. lxii. 180.)

Fig. 16.



Chemists are not agreed as to the order of electric energy in which the elements should be arranged. The following is that given by Berzelius, and may be viewed as approximative rather than rigidly exact:—Sulphur, nitrogen, and hydrogen scarcely occupy their true position in the series. The two former are less electro-negative than chlorine and fluorine, and hydrogen, I conceive, should occupy a prominent station among the electro-positive elements. All the bodies in the first series are — with regard to those in the second. In the first series each element is —, and in the second +, to all those which follow it.

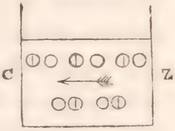
1. *Negative Electrics.*—Oxygen, sulphur, nitrogen, chlorine, iodine, fluorine, phosphorus, selenium, arsenic, chromium, molybdenum, tungsten, boron, carbon, antimony, tellurium, columbium, titanium, silicon, osmium, hydrogen.

2. *Positive Electrics.*—Potassium, sodium, lithium, barium, strontium, calcium, magnesium, glucinium, yttrium, aluminium, zirconium, manganese, zinc, cadmium, iron, nickel, cobalt, cerium, lead, tin, bismuth, uranium, copper, silver, mercury, palladium, platinum, rhodium, iridium, gold.

Theory of Chemical Decomposition.—Compounds are decomposed by galvanism, so far as is known, only when they are more or less fluid, that state being apparently necessary for giving mobility to the elements, which are otherwise chained down to one spot and prevented from separating. Davy's opinion, that an element is actually transferred beyond the place in which the decomposing compound exists, is untenable after the experiments of Faraday (page 113).

The facts adduced by the latter philosopher are inconsistent with the hypothesis of Davy, by which he accounted for chemical decomposition and transfer, namely, that attraction is exerted for the elements of compounds by the metallic conductors *a b*. The most feasible theory is that of Grotthus, of there being successive decompositions and recompositions in the line of particles lying between the electrodes. Let the upper part of fig. 17 represent a row of three particles of water lying between the electrodes *c z*, oxygen being represented by ○, and hydrogen by ⦶. A + current, in passing through them, is assumed to impart a kind of polar or magnetic virtue to the particles of oxygen and hydrogen, whereby affinity is weakened or destroyed on one side, and exalted on the other: each particle of hydrogen, for example, loses its attraction for the oxygen on its right side and quits it, but acquires an attraction for the oxygen on the left side and combines with it. Three particles of water thus yield, as in the lower part of fig. 17, two other particles which are generated; while the extreme particles of oxygen and hydrogen are set free. There is thus no transfer from one spot to another; the oxygen and hydrogen are set free at the place where they pre-existed; and they are evolved as gases, unless, by some secondary action, they should unite with the matter of the electrodes or with some element of the solution.

Fig. 17.



The preceding theoretical questions have been discussed on the assumption of electricity, as explained in the last section, being an independent principle susceptible of rapid motion from one body to another; and that the condition of a voltaic conducting wire is similar to that of a wire leading from the ground to the prime conductor of an electrical machine, or which connects the inner and outer surface of a charged Leyden phial, except that the voltaic current moves slowly, owing to its lower tension and the interposed imperfect conductor. Some conceive that what is called an electric current is not an actual transfer of any thing, but a process of induction among the molecules of a conductor passing progressively along it. Others, denying independent materiality to electricity, may ascribe it to a wave of vibrating matter, just as the phenomena of optics are explained by the undulatory theory. But whatever theory of the nature of electricity may be adopted, it seems necessary, after the experiments of Faraday on the identity of voltaic and common electricity, to admit that the nature of an electric and voltaic current is essentially the same.

PART II.

INORGANIC CHEMISTRY.

PRELIMINARY REMARKS.

In teaching a science such as chemistry, the details of which are numerous and complicated, it would be injudicious to follow the order of discovery, and proceed from individual facts to the conclusions which have been deduced from them. An opposite course is indispensable. It is necessary to discuss general principles in the first instance, in order to aid the beginner in remembering insulated facts, and in comprehending the explanations connected with them. The second part of this work will therefore commence with an explanation of the leading doctrines of the science. One inconvenience, indeed, arises from this method. It is often necessary, by way of illustration, to refer to facts of which the beginner is ignorant; and hence on some occasions more knowledge will be required for understanding a subject fully, than the reader may have at his command. But these instances will, it is hoped, be rarely met with; and when they do occur, the reader is advised to quit the point of difficulty, and return to the study of it when he shall have acquired more extensive knowledge of the details.

To the chemical history of each substance its chief physical characters will be added. A knowledge of these properties is not only advantageous in assisting the chemist to distinguish one body from another, but in many instances it is applied to uses still more important. The character called *specific gravity*, the meaning of which was explained at page 48, is of so much importance that the mode of determining it will be mentioned in this place. The process consists in weighing a body carefully, and then determining the weight of an equal bulk of water, the latter being regarded as unity. If, for example, a portion of water weigh nine grains, and the same bulk of another body 20 grains, its sp. gr. is determined by this formula;— as 9 : 20 : : 1 (assumed as the sp. gr. of water) to the fourth proportional 2·2222; so that the sp. gr. of any substance is found by dividing its weight by the weight of an equal volume of water. It is easy to discover the weight of equal bulks of water and any other liquid by filling a small bottle of known weight with each successively, and weighing them.* The method of obtaining the necessary data in case of a solid is somewhat different. The body is first weighed in air, is next suspended in water by means of a hair attached to the scale of the balance, and is then weighed again. The difference between the two weights gives the weight of a quantity of water equal to the bulk of the solid. This rule is founded on the hydrostatic law, that a solid body, immersed in any liquid, not only weighs less than it does in air, but the difference corresponds exactly to the weight of liquid which it displaces; and it is obvious that the liquid so displaced is exactly of the same dimensions as the solid. Another method is by the use of the bottle recommended for taking the sp. gr. of liquids. After weighing the bottle filled with water, a known weight of the solid is put into it, which of course displaces a quantity of water precisely equal to its own volume. The exact weight of the displaced water is found by weighing the bottle again, after its outer surface is made perfectly dry.

The determination of the sp. gr. of gaseous substances is an operation of much greater delicacy. From the extreme lightness of gases, it would be inconvenient to compare them with an equal bulk of water, and therefore atmospheric air is taken as the standard of comparison. The first step of the process is to ascertain the weight of a given volume of air. This is done by weighing a very light glass flask, furnished with a good stopcock, while full of air; and then weighing it a second time, after the air has been withdrawn by means of the air-pump. The difference between the two weights gives the information required. According to the observation of Prout, 100 cubic inches of pure and dry atmospheric air, at the temperature of 60^0 and when the barometer stands at 30 inches, weigh 31·0117 grains. By a similar method the weight of any other gas may be determined, and its sp. gr. be inferred accordingly. For instance, suppose 100 cubic inches of oxygen gas are found to weigh 34·109 grains, its sp. gr. will be thus deduced; as 31·0117 : 34·109 : : 1 (the sp. gr. of air) : 1·1025, the sp. gr. of oxygen.

There are four circumstances to which particular attention must be paid in taking the specific gravity of gases:—

1. The gas should be perfectly pure, otherwise the result cannot be accurate.

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* Bottles are prepared for this purpose by the philosophical instrument makers.

2. Due regard must be had to its hygrometic condition. If it is saturated with moisture, the necessary correction may be made by the formula of page 49 ; or it may be dried by the use of substances which have a powerful attraction for moisture, such as chloride of calcium, quicklime, or fused potassa.

3. As the bulk of gaseous substances, owing to their elasticity and compressibility, is dependent on the pressure to which they are exposed, no two observations admit of comparison, unless made under the same elevation of the barometer. It is always understood, in taking the sp. gr. of a gas, that the barometer must stand at 30 inches, by which means the operator is certain that each gas is subject to equal degrees of compression. An elevation of thirty inches is called the standard height ; and if the mercurial column be not of that length at the time of performing the experiment, the error arising from this cause must be corrected by calculation. It has been established by experiment that the bulk of gases is inversely as the pressure to which they are subject. Thus, 100 measures of air, under the pressure of 30 inches of mercury, will dilate to 200 measures, if the pressure be diminished by one half; and will be compressed to 50 measures, when the pressure is double, or equal to a mercurial column of 60 inches. The correction for the effect of pressure may therefore be made by the rule of three, as will appear by an example. If a certain portion of gas occupy the space of 100 measures at 29 inches of the barometer, its bulk at 30 inches may be obtained by the following proportion ; as 30 : 29 : : 100 : 96·66.

It is understood that the temperature of the mercurial column is constant: if not so, correction must be made for the change in the volume of the mercury produced by change of temperature, on the principle laid down at page 23.

4. For a similar reason the temperature should always be the same. The standard or mean temperature is 60° ; and if the gas be admitted into the weighing-flask when the thermometer is above or below that point, the formula of page 25 should be employed for making the necessary correction.

The first attempt to form a systematic chemical nomenclature was made by Lavoisier, Berthollet, Guyton de Morveau, and Fourcroy, soon after the discovery of oxygen gas. To avoid an undue use of new terms, the known elements and the most familiar compound bodies were allowed to retain the names which usage had assigned to them. The newly-discovered elements were named from some striking property. Thus, oxygen, from *οξυς* acid, and *γενναειν* to generate, was so called from a belief that it is the universal cause of acidity ;

and the term hydrogen, from ὕδωρ water, and γεννᾶειν, was applied to the inflammable element of water. The compounds into which oxygen enters were termed *acids* or *oxides*, according as they do or do not possess acidity. The name of an acid was derived from the substance acidified by the oxygen, to which was added the termination in *ic*. Thus sulphur*ic* and carbon*ic* acids signified compounds of sulphur and carbon with oxygen. Should sulphur or any other body form two acids, the name of that containing least oxygen was made to terminate in *ous*, as sulphur*ous* acid. The termination in *uret* was applied to compounds of the simple non-metallic substances with each other, with a metal, or with a metallic oxide: thus, sulph*uret* and carb*uret* of iron signify compounds of sulphur and carbon with iron. The general term *salt* comprehended compounds of acids with alkaline bases, and the names of the salts were so contrived as to indicate the substances contained in them. If the acid contain a maximum of oxygen, the name of the salt terminated in *ate*; if a minimum, the termination in *ite* was used: thus, sulph*ate* and phosph*ate* of potassa are salts of sulphur*ic* and phosphor*ic* acids; while the terms sulph*ite* and phosph*ite* of potassa denote salts of that alkali with sulphur*ous* and phosphor*ous* acids.

These instances suffice to exhibit the principles by which the framers of the nomenclature were guided. Their object was to apply similar names to similar things, and so to construct those names as to indicate the nature or composition of the bodies to which they were attached. The same views have been acted on by succeeding chemists, who with this intention have availed themselves of the laws of definite combination. The more essential parts of this method, as adopted in these elements, are the following:—The names of newly-discovered elements are selected from some obvious property: thus, chlorine and iodine were so called from their colour. The termination of a name is rendered similar to those of nearly allied substances: thus, iod*ine*, and fluor*ine* received that termination from their analogy to chlorine; the compounds of chlorine, iodine, bromine, and fluorine, from their relations to oxygen, are termed chlor*ides*, iod*ides*, &c.; and the compounds of selenium, and other similar inflammables, are called seleni*urets*, from their analogy to sulph*urets* and phosphurets. The names of metals, except some, as iron and tin, whose names have been sanctioned by usage, terminate in *um*, as potassium and titanium. The names of alkaline bases, when expressed by one word, terminate in *a*, as potassa and morphia. When one substance forms with oxygen three or more acids, a Greek preposition is usually prefixed to indicate the relative quantity of oxygen: thus, *hypo*nitrous acid contains less oxygen than the nitrous: *hyper*nitrous would apply to an acid with more oxygen than the nitrous; and *hypo*sulphur*ic* acid indicates an acid with less oxygen than the sulphuric, and more than the sulphurous. *Per* is sometimes prefixed with the same intention as *hyper*: thus, *per*chloric acid contains more oxygen than the chloric. Different oxides of the same metal are distinguished by derivates from the Greek or Latin. An oxide consisting of an equivalent of each element is denoted either by the term oxide without any affix, or by *prot*oxide (πϱωτος, first); the highest grade is the *per*oxide; and the intermediate grades are distinguished by Latin numerals expressing the number of equivalents of oxygen combined with one equivalent of the metal, such as, *bin*oxide, *ter*oxide, &c. Sesqui, one and a half, is used to indicate the relation of 1 to 1½, or 2 to 3, as in the sesquioxide of iron or cobalt. The Greek numerals *dis*, *tris*, *tetrakis*, are prefixed in like manner to denote oxides formed with one equivalent of oxygen, and two, three, or more equivalents of a metal. More complex ratios, such as 3 eq. of a metal to 4 eq. of oxygen, are denoted by a fraction, $\frac{4}{3}$, placed before the name of the oxide.

The same system is extended not merely to the union of elements generally with each other, but to compounds of a more complex nature, such as the salts. To a salt formed of an equivalent of the acid and alkali, its generic name without other addition is applied; but if two or more equivalents of the acid are attached to one eq. of the base, or two or more equivalents of the base to one eq. of the acid, a numeral is prefixed so as to indicate its composition. The two salts of sulphuric acid and potassa are called sulphate and *bi*sulphate; the first containing an eq. of the acid and alkali, and the latter one eq. of the alkali to two of the acid. The three salts of oxalic acid and potassa are termed the oxalate, *bin*oxalate, and *quadr*oxalate of potassa; because one eq. of the alkali is united with one eq. of acid in the first salt, with two in the second, and with four in the third. In the chromate and *di*chromate of oxide of lead, 1 eq. of the acid is united with 1 eq. of oxide in the former, and with 2 in the latter. The term salt has of late received considerable extension, being now applied to compounds analogous to common salt in constitution, though not formed of an acid and alkali. The grounds on which this has been done, and the nomenclature introduced in consequence, are explained in the section of the salts.—In speaking of salts of metallic oxides, many chemists are in the practice, for the sake of brevity, of mentioning the name of the metals only. Thus, in the expressions *sulphates of silver and lead*, the *oxide* of silver and *oxide* of lead are to be understood. The present comprehensive sense in which the word *salt* is used begins to render this practice objectionable.

The generic part of the name of a compound is usually formed from that ingredient which is considered the most highly electro-negative. Thus, to compounds of oxygen and chlorine, chlorine and iodine, iodine and sulphur, sulphur and potassium, in which the first of each pair is the electro-negative element, the correct appellations are oxides of chlorine, chloride of iodine, iodide of sulphur, sulphuret of potassium ; and not chloride of oxygen, iodide of chlorine, sulphuret of iodine, and potassiuret of sulphur. This practice is invariably observed in this treatise.

Convenient and philosophical as this nomenclature may at first appear, its principles are now felt to be far from coextensive with the science. It much needs extension and modification. To many of the complex compounds known to chemists it is impracticable to apply convenient names correctly expressive of their constitution ; and this has led to the use of those symbolic characters which have become general among chemists, and which are essential to the present state of chemistry. The mode of employing such notation will be explained in the second section of this part.

SECTION I.

AFFINITY.

All chemical phenomena are owing to Affinity or Chemical Attraction. It is the basis on which the science of chemistry is founded. It is, as it were, the instrument which the chemist employs in all his operations, and hence it forms the first and leading object of his study.

Affinity is exerted between the minutest particles of different kinds of matter, causing them to combine so as to form new bodies endowed with new properties. It acts only at insensible distances ; in other words, apparent contact, or the closest proximity, is necessary to its action. Everything which prevents such contiguity is an obstacle to combination ; and any force which increases the distance between particles already combined, tends to separate them permanently from each other. In the former case, they do not come within the sphere of their mutual attraction ; in the latter, they are removed out of it. It follows, therefore, that though affinity is regarded as a specific power distinct from the other forces which act on matter, its action may be promoted, modified, or counteracted by them ; and consequently, in studying the phenomena produced by affinity, it is necessary to inquire into the conditions that influence its operation.

The most simple instance of the exercise of chemical attraction is afforded by the admixture of two substances. Water and sulphuric acid, or water and alcohol, combine readily. On the contrary, water shows little disposition to unite with ether, and still less with oil; for, however intimately their particles may be mixed together, they are no sooner left at rest than the ether separates almost entirely from the water, and a total separation takes place between that fluid and the oil. Sugar dissolves very sparingly in alcohol, but to any extent in water; while camphor is dissolved in a very small degree by water, and abundantly by alcohol. It appears, from these examples, that chemical attraction is exerted between different bodies with different degrees of force. There is sometimes no proof of its existence at all; between some substances it acts very feebly, and between others with great energy.

Simple combination of two substances is a common occurrence; of which the solution of salts in water, the combustion of phosphorus in oxygen gas, and the neutralization of a pure alkali by an acid, are instances. But the phenomena are often more complex. The formation of a new compound is often attended by the destruction of a preexisting one; as when some third body acts on a compound, for one element of which it has a greater affinity than they have for one another. Thus, oil has an affinity for the volatile alkali, ammonia, and will unite with it, forming a soapy substance called a liniment. But the ammonia has a still greater attraction for sulphuric acid; and hence, if the acid be added to the liniment, the alkali will quit the oil, and unite by preference with the acid. If a solution of camphor in alcohol be poured into water, the camphor will be set free because the alcohol combines with the water. Sulphuric acid, in like manner, separates baryta from nitric acid. Combination and decomposition occur in each of these cases;—combination of sulphuric acid with ammonia, of water with alcohol, of baryta with sulphuric acid;—decomposition of the compounds formed of oil and ammonia, of alcohol and camphor, of nitric acid and baryta. These are examples of what Bergmann called *single elective affinity*; — elective, because a substance manifests, as it were, a choice for one of two others, uniting with it by preference, and to the exclusion of the other. Many of the decompositions that occur in chemistry are instances of single elective affinity.

The order in which these decompositions take place has been expressed in tables; of which the following, drawn up by Geoffroy, is an example:—

Sulphuric acid.

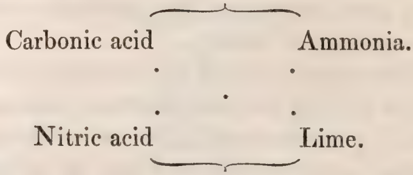
Baryta,
Strontia,
Potassa,
Soda,
Lime,
Ammonia,
Magnesia.

This table signifies, first, that sulphuric acid has an affinity for the substances placed below the horizontal line, and may unite separately with each; and, secondly, that the bases of the salts so formed will be separated from the acid by adding any of the alkalies or earths which stand above it in the column. Thus, ammonia will separate magnesia, lime ammonia, and potassa lime; but none can withdraw baryta from sulphuric acid, nor can ammonia or magnesia decompose sulphate of lime, though strontia or baryta will do so. Bergmann conceived that these decompositions are solely determined by chemical attraction, and that consequently the order of decomposition represents the comparative forces of affinity; and this view, from the simple and natural explanation it affords of the phenomenon, was for a time very generally adopted. But Bergmann was in error. It does not necessarily follow, because lime separates ammonia from sulphuric acid, that the lime has a greater attraction for the acid than the volatile alkali. Other causes are in operation which modify the action of affinity to such a degree, that it is impossible to discover how much of the effect is owing to that power. It is conceivable that ammonia may in reality have a stronger attraction for sulphuric acid than lime, and yet that the latter, from the great influence of disturbing causes, may succeed in decomposing sulphate of ammonia.

The propriety of the foregoing remark will appear from the following example:—When a stream of hydrogen gas is passed over oxide of iron heated to redness, the oxide is reduced to the metallic state, and water is generated. On the contrary, when watery vapour is brought into contact with red-hot metallic iron, the oxygen of the water quits the hydrogen, and combines with the iron. It follows from the result of the first experiment, according to Bergmann, that hydrogen has a stronger attraction than iron for oxygen; and from that of the second, that iron has a greater affinity for oxygen than hydrogen. But these inferences are incompatible with each other. The affinity of oxygen for the two elements, hydrogen and iron, must either be equal or unequal. If equal, the result of both experiments was determined by modifying circumstances; since neither of these substances ought on this supposition to take oxygen from the other. But if the forces are unequal, the decomposition in one of the experiments must have been determined by extraneous causes, in direct opposition to the tendency of affinity.

The fallacy of Bergmann's opinion was detected by Berthollet. He first showed that the relative forces of chemical attraction cannot always be determined by observing the order in which substances separate each other when in combination, and that the tables of Geoffroy are merely tables of decomposition, not of affinity. He likewise traced all the various circumstances that modify the action of affinity, and gave a consistent explanation of the mode in which they operate. Berthollet went even a step further. He denied the existence of elective affinity as an invariable force, capable of effecting the perfect separation of one body from another, and maintained that all the instances of complete decomposition attributed to elective affinity are in reality determined by one or more of the collateral circumstances that influence its operation. But here this acute philosopher went too far. Bergmann erred in supposing the result of chemical action to be in every case owing to elective affinity; but Berthollet ran into the opposite extreme in declaring that the effects formerly ascribed to that power are never produced by it. That chemical attraction is exerted between bodies with different degrees of energy, is, I apprehend, indisputable. Water has a much greater affinity for hydrochloric acid and ammoniacal gases than for carbonic and hydrosulphuric acids, and for these than for oxygen and hydrogen. The attraction of lead for oxygen is greater than that of silver for the same substance. The disposition of gold and silver to combine with mercury is greater than the attraction of platinum and iron for that fluid. As these differences cannot be accounted for by the operation of any modifying causes, we must admit a difference in the force of affinity in producing combination. It is equally clear that in some instances the separation of bodies from one another can only be explained on the same principle. No one, I conceive, will contend that the decomposition of hydriodic acid by chlorine, or of hydrosulphuric acid by iodine, is determined by the concurrence of any modifying circumstances.

Affinity is the cause of changes still more complicated than those which have just been considered. In a case of single elective affinity, three substances only are present, and two affinities are in play. But it frequently happens that two compounds are mixed together, and four different affinities brought into action. The changes that may or do occur under these circumstances may be studied by aid of a diagram. Thus, in mixing together a solution of carbonate of ammonia and nitrate of lime, their mutual action may be represented in the following manner:—



Each of the acids has an attraction for both bases, and hence it is possible either that the two salts should continue as they were, or that an interchange of principles should ensue, giving rise to two new compounds,—carbonate of lime and nitrate of ammonia. According to the views of Bergmann, the result is solely dependent on the comparative strength of affinities. If the affinity of carbonic acid for ammonia, and of nitric acid for lime, exceed that of carbonic acid for lime, added to that of nitric acid for ammonia, then will the two salts experience no change whatever; but if the latter affinities preponderate, then, as does actually happen in the present example, both the original salts will be decomposed, and two new ones generated. Two decompositions and two combinations take place, being an instance of what is called *double elective affinity*. Kirwan applied the terms *quiescent* and *divellent* to denote the tendency of the opposing affinities,—the action of the former being to prevent a change, the latter to produce it.

The doctrine of double elective affinity was assailed by Berthollet on the same ground and with the same success as in the case of single electrive attraction. He succeeded in proving that the effect cannot always be ascribed to the sole influence of affinity. For, to take the example already adduced, if carbonate of ammonia decompose nitrate of lime by the mere force of a superior attraction, it is manifest that carbonate of lime ought never to decompose nitrate of ammonia. But if these two salts are mixed in a dry state and exposed to heat, double decomposition does take place, carbonate of ammonia and nitrate of lime being formed; and therefore, if the change in the first example was produced by chemical attraction alone, that in the second must have occurred in direct opposition to that power. It does not follow, however, because the result is sometimes determined by modifying conditions, that it must always be so. I apprehend that the decomposition of the solid cyanuret of mercury by hydrosulphuric acid gas, which takes place even at a low temperature, cannot be ascribed to any other cause than a preponderance of the divellent over the quiescent affinities.

ON THE CHANGES THAT ACCOMPANY CHEMICAL ACTION.

The leading circumstance that characterises chemical action is the loss of properties experienced by the combining substances, and the appearance of new ones in the product of their combination. The change of property is sometimes inconsiderable. In a solution of sugar or salt in water, and in mixtures of water with alcohol or sulphuric acid, the compound retains so much of the character of its constituents, that there is no difficulty in recognising their presence. But more generally the properties of one or both of the combining bodies disappear entirely. One would not suppose from its appearance, that water is a compound body ; much less that it is composed of two gases, oxygen and hydrogen, neither of which, when uncombined, has ever been compressed into a liquid. Hydrogen is one of the most inflammable substances in nature, and yet water cannot be set on fire : oxygen, on the contrary, enables bodies to burn with great brilliancy, and yet water extinguishes combustion. The alkalies and earths were regarded as simple till Davy proved them to be compound ; and certainly they evince no sign whatever of containing oxygen and a metal. Numerous examples of a similar kind are afforded by the mutual action of acids and alkalies. Sulphuric acid and potassa, for example, are highly caustic. The former is intensely sour, reddens the blue colour of vegetables, and has a strong affinity for alkaline substances ; the latter has a pungent taste, converts the blue colour of vegetables to green, and combines readily with acids. On adding these principles cautiously to each other, a compound results called a *neutral salt*, which does not in any way affect the colouring matter of plants, and in which the other distinguishing features of the acid and alkali can no longer be perceived. They appear to have destroyed the properties of each other, and are hence said to *neutralize* one another.

The other phenomena that accompany chemical action are changes of density, temperature, form, and colour.

1. It is observed that two bodies rarely occupy, after combination, the same space which they possessed separately. In general their bulk is diminished, so that the sp. gr. of the new body is greater than the mean of its components. Thus a mixture of 100 measures of water and an equal quantity of sulphuric acid does not occupy the space of 200 measures, but considerably less. A similar contraction frequently attends the combination of solids. Gases often experience a remarkable condensation when they unite. The elements of olefiant gas, for instance, would expand to four times the bulk of that

compound, if they were suddenly to become free, and assume the gaseous form. But the rule is not without exception. The reverse happens in some metallic compounds; and there are examples of combination between gases without any change of bulk.

2. A change of temperature generally accompanies chemical action. Heat is evolved either when there is a diminution in the bulk of the combining substances without change of form, or when a gas is condensed into a liquid, or a liquid becomes solid. The heat caused by mixing sulphuric acid with water is an instance of the former; and the common process of slaking lime, during which water loses its liquid form in combining with that earth, is an example of the latter. The rise of temperature in these cases is obviously referrible to diminished sp. heat in the new compound; but intense heat sometimes accompanies chemical action under circumstances in which an explanation founded on a change of sp. heat is inadmissible. At present it is enough to have stated the fact; its theory will be discussed under the subject of combustion. The production of cold seldom or never takes place during combination, except when heat is rendered insensible by the conversion of a solid into a liquid, or a liquid into a gas. All the frigorific mixtures act in this way.

3. The changes of form that attend chemical action are exceedingly various. The combination of gases may give rise to a liquid or a solid; solids sometimes become liquid, and liquids solid. Several familiar chemical phenomena, such as detonation, effervescence, and precipitation, are owing to these changes. The sudden evolution of a large quantity of gaseous matter causes an explosion, as when gunpowder detonates. The slower disengagement of gas produces effervescence, as when marble is put into hydrochloric acid. Precipitation is owing to the formation of a new body which happens to be insoluble in the liquid in which its elements were dissolved, and which therefore falls, or is *precipitated* to the bottom in the solid form.

4. Chemical action is frequently attended by change of colour. No uniform relation has been traced between the colour of a compound and that of its elements. Iodine, whose vapour is of a violet hue, forms a beautiful red compound with mercury, and a yellow one with lead. The black oxide of copper generally gives rise to green and blue coloured salts; while the salts of the oxide of lead, which is itself yellow, are for the most part colourless. The colour of precipitates is a very important study, as it supplies a character by which many substances may be distinguished.

ON THE CIRCUMSTANCES THAT MODIFY AND INFLUENCE THE OPERATION OF AFFINITY.

Of the conditions which are capable of promoting or counteracting the tendency of chemical attraction, the following are the most important: cohesion, elasticity, quantity of matter, gravity, and contact with other bodies. To these may be added the agency of the imponderables.

Cohesion.—The first obvious effect of cohesion is to oppose affinity, by impeding or preventing that mutual penetration and close proximity of the particles of different bodies, which is essential to the successful exercise of their attraction. Bodies seldom act chemically in their solid state; their molecules do not come within the sphere of attraction, and therefore combination cannot take place, although their affinity may in fact be considerable. Liquidity, on the contrary, favours chemical action; it permits the closest possible approximation, while the cohesive power is comparatively so trifling as to oppose no appreciable barrier to affinity.

Cohesion may be diminished in two ways,—by mechanical division, or by the application of heat. The former aids by increasing the extent of surface; but it is not of itself in general sufficient, because the particles, however minute, still retain that degree of cohesion which constitutes solidity. Heat acts with greater effect, and never fails in promoting combination, whenever the cohesive power is a barrier to it. Its intensity should always be so regulated as to produce liquefaction. The fluidity of one of the substances frequently suffices for effecting chemical union, as is proved by the facility with which water dissolves many salts and other solid bodies. But the cohesive force is still in operation; for a solid is commonly dissolved in greater quantity when its cohesion is diminished by heat. The reduction of both substances to the liquid state is the best method for ensuring chemical action. The slight degree of cohesion possessed by liquids does not appear to cause any impediment to combination; for they commonly act as energetically on each other at low temperatures, or at a temperature just sufficient to cause perfect liquefaction, as when their cohesive power is still further diminished. It seems fair to infer, therefore, that very little, if any, affinity exists between two bodies which do not combine when they are intimately mixed in a liquid state.

The phenomena of crystallization are owing to the ascendency of cohesion over affinity. When a large quantity of salt has been dissolved in water by the aid of heat, part of the saline matter generally separates as the solution cools, because the cohesive power of the salt then becomes comparatively too powerful for chemical attraction. Its particles begin to cohere together, and are deposited in crystals, the process of crystallization continuing till it is arrested by the affinity of the liquid. A similar change happens when a solution made in the cold is gradually evaporated. The cohesion of the saline particles is no longer counteracted by the affinity of the liquid, and the salt therefore assumes the solid form.

Cohesion plays a still more important part. It sometimes determines the result of chemical action, probably even in opposition to affinity. Thus, on mixing together a solution of two acids and one alkali, of which two salts may be formed, one soluble and the other insoluble, the alkali will unite with that acid with which it forms the insoluble compound, to the total exclusion of the other. This is one of the modifying circumstances employed by Berthollet to account for the phenomena of single elective attraction, and is certainly applicable to many of the instances to be found in the tables of affinity. When, for example, hydrochloric acid, sulphuric acid, and baryta are mixed together, sulphate of baryta is formed in consequence of its insolubility. Lime, which yields an insoluble salt with carbonic acid, separates that acid from ammonia, potassa, and soda, with all of which it makes soluble compounds.

A similar explanation may be given of many cases of double elective attraction. On mixing together in solution four substances, A, B, C, D, of which it is possible to form four compounds, AB and CD, or AC and BD, that compound will certainly be produced which happens to be insoluble. Thus, sulphuric acid, soda, nitric acid, and baryta may give rise either to sulphate of soda and nitrate of baryta, or to sulphate of baryta and nitrate of soda; but the first two salts cannot exist together in the same liquid, because the insoluble sulphate of baryta is instantly generated, and its formation necessarily causes the nitric acid to combine with the soda. In like manner, a solution of nitrate of lime is decomposed by carbonate of ammonia, in consequence of the insolubility of carbonate of lime.

To comprehend the manner in which cohesion acts in these instances, it is necessary to consider what takes place when in the same liquid two or more compounds are brought together, which do not give rise to an insoluble substance. Thus, on mixing solutions of sulphate of potassa and nitrate of soda, no precipitate ensues; because the salts capable of being formed by double decomposition, sulphate of soda and nitrate of potassa, are likewise soluble. In this case it is possible either that each acid may be confined to one base, so as to constitute two neutral salts; or that each acid may be divided between both bases, yielding four neutral salts. It is difficult to decide this point in an unequivocal manner: but, judging from many chemical phenomena, there can, I apprehend, be no doubt that the arrangement last mentioned is the most frequent, and is probably universal whenever the relative forces of affinity are not very unequal. When two acids and two bases meet together in neutralizing proportion, it may therefore be inferred, that each acid unites with both the bases in a manner regulated by their respective forces of affinity, and that four salts are contained in solution. In like manner, the presence of three acids and three bases will give rise to nine salts; and when four of each are present, sixteen salts will be produced. This view affords the most plausible theory of the constitution of mineral waters, and of the products which they yield by evaporation.

The influence of insolubility in determining the result of chemical action may be readily explained on this principle. If nitric acid, sulphuric acid, and baryta are mixed together in solution, the base may be conceived to be at first divided between the two acids, and nitrate and sulphate of baryta to be generated. The latter, being insoluble, is instantly removed beyond the influence of the nitric acid, so that for an instant nitrate of baryta and free sulphuric acid remain in the liquid: but as the base left in solution is again divided between the two acids, a fresh quantity of the insoluble sulphate is generated; and this process of partition continues, until either the baryta or the sulphuric acid is withdrawn from the solution. Similar changes ensue when nitrate of baryta and sulphate of soda are mixed.

The separation of salts by crystallization from mineral waters or other saline mixtures is explicable by a similar mode of reasoning. Thus, on mixing nitrate of potassa and sulphate of soda, four salts, according to this view, are generated,—namely, the sulphates of soda and potassa, and the nitrates of those bases; and if the solution be allowed to evaporate gradually, a point at length arrives when the least soluble of these salts, the sulphate of potassa, will be disposed to crystallize. As soon as some of its crystals are deposited, and thus withdrawn from the influence of the other salts, the constituents of these undergo a new arrangement, whereby an additional quantity of sulphate of potassa is generated; and this process continues until the greater part of the sulphuric acid and potassa has combined, and the compound is removed by crystallization. If the difference in solubility is considerable, the separation of salts may be often rendered very complete by this method.

The efflorescence of a salt is sometimes attended with a similar result. If carbonate of soda and chloride of calcium are mingled together in solution, the insoluble carbonate of lime subsides. But if carbonate of lime and sea-salt are mixed in the solid state, and a certain degree of moisture is present, carbonate of soda and chloride of calcium are slowly generated; and since the former, as soon as it is formed, separates itself from the mixture by efflorescence, its production continues progressively. The efflorescence of carbonate of soda, which is sometimes seen on old walls, or which in some countries is found on the soil, appears to have originated in this manner.

Elasticity.—From the obstacle which cohesion puts in the way of affinity, the gaseous state, in which the cohesive power is wholly wanting, might be expected to be peculiarly favourable to chemical action. The reverse, however, is the fact. Bodies evince little disposition to unite when presented to each other in the elastic form. Combination does indeed sometimes take place, in consequence of a very energetic attraction; but examples of an opposite kind are much more common. Oxygen and hydrogen gases, and chlorine and hydrogen, though their mutual affinity is very powerful, may be preserved together for any length of time without combining. This want of action seems to arise from the distance between the particles preventing that close approximation which is so necessary to the successful exercise of affinity. Hence many gases cannot be made to unite directly, which nevertheless combine readily while in their *nascent* state; that is, while in the act of assuming the gaseous form by the decomposition of some of their solid or fluid combinations.

Elasticity operates likewise as a decomposing agent. If two gases, the reciprocal attraction of which is feeble, suffer considerable condensation when they unite, the compound will be decomposed by very slight causes. Chloride of nitrogen, which is an oil-like liquid, composed of the two gases, chlorine and nitrogen, affords an apt illustration of this principle, being distinguished for its remarkable facility of decomposition. Slight elevation of temperature, by increasing the natural elasticity of the two gases, or contact of substances which have an affinity for either of them, produces immediate explosion.

Many familiar phenomena of decomposition are owing to elasticity. All compounds that contain a volatile and a fixed principle are liable to be decomposed by a high temperature. The expansion occasioned by heat removes the elements of the compound to a greater distance from each other, and thus, by diminishing the force of chemical attraction, favours the tendency of the volatile principle to assume the form which is natural to it. The evaporation of water from a solution of salt is an instance of this kind.

Many solid substances which contain water in a state of intimate combination part with it in a strong heat, in consequence of the volatile nature of that liquid. The separation of oxygen from some metals, by heat alone, is explicable on the same principle.

From these and some preceding remarks, it appears that the influence of heat over affinity is variable; for at one time it promotes chemical union, and opposes it at another. Its action, however, is always consistent. Whenever the cohesive power is an obstacle to combination, heat favours affinity either by diminishing the cohesion of a solid, or by converting it into a liquid. As the cause of the gaseous state, on the contrary, it keeps at a distance particles which would otherwise unite; or, by producing expansion, it tends to separate from one another substances which are already combined. There is one effect of heat which seems somewhat anomalous; namely, the combination which ensues in gaseous explosive mixtures on the approach of flame. The explanation given by Berthollet is probably correct, — that the sudden dilatation of the gases in the immediate vicinity of the flame acts as a violent compressing power to the contiguous portions, and thus brings them within the sphere of their attraction.

Some of the decompositions, which were attributed by Bergmann to the sole influence of elective affinity, may be ascribed to elasticity. If three substances are mixed together, two of which can form a compound which is less volatile than the third, the last will, in general, be completely driven off by the application of heat. The decomposition of the salts of ammonia by the pure alkalies or alkaline earths may be adduced as an example; and, for a like reason, all the carbonates are decomposed by nitric acid, and all the nitrates by sulphuric acid. This explanation applies equally well to some cases of double decomposition. It explains, for instance, why dry carbonate of lime will decompose nitrate of ammonia by the aid of heat; for carbonate of ammonia is more volatile than the nitrate either of ammonia or lime.

The influence of elasticity in determining the results of chemical action in these instances seems owing to the same cause which enables insolubility to be productive of similar effects. Thus, on mixing nitrate of ammonia with lime, the acid is divided between the two bases; some ammonia becomes free, which, in consequence of its elasticity, is entirely expelled by a gentle heat. The acid of the remaining nitrate of ammonia is again divided between the two bases; and if a sufficient quantity of lime is present, the ammoniacal salt will be completely decomposed. In like manner, the decomposition of potassa may be effected by iron, though the affinity of this metal for oxygen seems much inferior to that of potassium for oxygen. If potassa in the fused state be brought in contact with metallic iron at a white heat, the oxygen is divided between the two metals, and a portion of potassium set at liberty. But as potassium is volatile at a white heat, it is expelled at the instant of reduction; and thus, by its influence being withdrawn, an opportunity is given for the decomposition of an additional quantity of potassa.

Quantity of Matter.—The influence of quantity of matter over affinity is universally admitted. If one body, A, unites with another, B, in several proportions, that compound will be most difficult of decomposition which contains the smallest quantity of B. Of the three oxides of lead, for instance, the peroxide parts most easily with its oxygen by the action of heat; a higher temperature is required to decompose the red oxide; and the protoxide will bear the strongest heat of our furnaces without losing a particle of its oxygen.

The influence of quantity over chemical attraction may be further illustrated by the phenomena of solution. When equal weights of a soluble salt are added in succession to a given quantity of water, which is capable of dissolving almost the whole of the salt employed, the first portion of the salt will disappear more readily than the second, the second than the third, the third than the fourth, and so on. The affinity of the water for the saline substance diminishes with each addition, till at last it is so weakened as to be unable to overcome the cohesion of the salt. The process then ceases, and a saturated solution results.

Quantity of matter is employed advantageously in many chemical operations. If a chemist wishes to displace a metallic oxide from an acid by the superior affinity of potassa for the latter, he frequently uses rather more of the alkali than is sufficient for neutralizing the acid. He employs an excess of the alkali, in order the more effectually to bring every particle of the substance to be decomposed in contact with the decomposing agent.

But Berthollet has attributed much greater influence to quantity of matter. It was the basis of his doctrine, developed in the *Statique Chimique*, that bodies cannot be wholly separated from each other by the affinity of a third substance for one element of a compound; and to explain why a superior chemical attraction does not produce the effect which might be expected from it, he contended that quantity of matter compensates for a weaker affinity. From the co-operation of several disturbing causes, Berthollet perceived that the force of affinity cannot be estimated with certainty by observing the order of decomposition; and he therefore had recourse to another method. He supposed the affinity of different acids for the same alkali to be in the inverse ratio of the ponderable quantity of each which is necessary for neutralizing equal quantities of the alkali. Thus, if two parts of one acid, A, and one part of another acid, B, are required to neutralize equal quantities of the alkali, C, it was inferred that the affinity of B for C was twice as great as that of A. He conceived, further, that as two parts of A produce the same neutralizing effect as one part of B, the attraction exerted by any alkali towards two parts of A ought to be precisely the same as for the one part of B; and he hence concluded that there is no reason why the alkali should prefer the small quantity of one to the large quantity of the other. On this he founded the principle that quantity of matter compensates for force of attraction.

Berthollet has here obviously confounded two things, namely, force of attraction and neutralizing power, which are really distinct. The relative weights of hydrochloric and sulphuric acids required to neutralize an equal quantity of any alkali, or, in other words, their capacities of saturation, are as 36·4 to 40, a ratio which remains constant with respect to all other alkalies. The affinity of these acids, according to Berthollet's rule, will be expressed by the inverse ratio of these numbers. But in taking this estimate, we have to make three assumptions, each of which is disputable. There is no proof, in the first place, that hydrochloric acid has a greater affinity for an alkali, such as potassa, than sulphuric acid. Such an inference would be directly opposed to the general opinion founded on the order of decomposition; and though that order, as we have shown, is by no means a satisfactory test of the strength of affinity, it would be improper to adopt an opposite conclusion without having good reasons for so doing. Secondly, were it established that hydrochloric acid has the greater affinity, it does not follow that the attraction of those acids for potassa is in the inverse ratio of 36·4 to 40. And, thirdly, supposing this point settled, it is very improbable that the ratio of their affinities for one alkali will apply to all others; analogy would lead us to anticipate the reverse. Independently of these objections, Dulong has found that the principle of Berthollet is not in accord with the results of experiment.

Gravity.—The influence of gravity is perceptible when it is wished to make two substances unite, the densities of which are different. In a case of simple solution, a larger quantity of saline matter is found at the bottom than at the top of the liquid, unless the solution shall have been well mixed subsequently to its formation. In making an alloy of two metals which differ in density, a larger quantity of the heavier metal will be found at the lower than in the upper part of the compound, unless great care be taken to counteract the tendency of gravity by agitation. This force obviously acts, like the cohesive power, in preventing a sufficient degree of approximation.

Contact with other bodies.—The influence of contact of different substances in modifying affinity is observable either in the increased or diminished energy of chemical action. The former is always the result of a galvanic current, and has been treated of elsewhere: the latter is produced by the interposition of an indifferent body by which others are removed out of the sphere of their mutual action. Thus, on immersing a fragment of pure zinc into dilute sulphuric acid the chemical action is no sooner commenced than it is checked by the hydrogen which is liberated; this is effected by the minute globules of the gas collecting upon the surface of the zinc, and adhering firmly to it, preventing the zinc and dilute acid from coming into that close contact which is essential to chemical action. Some means must therefore be used to remove this intervening film of hydrogen, if a continuous action be desired: this is effected when the common zinc of commerce is used by the minute portions of other metals present in it as impurities, by which small but numerous galvanic currents are excited, and by their action the hydrogen is collected and makes it escape as globules of gas.

Imponderables.—The influence which heat exerts over chemical phenomena, and the modes in which it operates, have been already discussed. The chemical agency of galvanism has also been described. The effects of light will be most conveniently stated in other parts of the work. Electricity is frequently employed to produce the combination of gases with one another, and in some instances to separate them. It appears to act by the heat which it occasions, and therefore on the same principle as flame.

On the measure of affinity.—As the foregoing observations prove that the order of decomposition is not always a satisfactory measure of affinity, it becomes a question whether there are any means of determining the comparative forces of chemical attraction. When no disturbing causes operate, the phenomena of decomposition afford a sure criterion; but when the conclusions obtained in this way are doubtful, assistance may be frequently derived from other sources. The surest indications are procured by observing the tendency of different substances to unite with the same body under the same circumstances, and subsequently marking the comparative facility of decomposition when the compounds so formed are exposed to the same decomposing agent. Thus, on exposing silver, lead, and iron, to air and moisture, the iron soon rusts, the lead is oxidized in a slight degree only, and the silver resists oxidation altogether. Iron is hence inferred to have the greatest affinity for oxygen, lead next, and silver the least. This conclusion is supported by concurring observations of a like nature, and confirmed by the circumstances under which the oxides of those metals part with their oxygen. Oxide of silver is reduced by heat only; and oxide of lead is decomposed by charcoal at a lower temperature than oxide of iron.

It is inferred from the action of heat on the carbonates of potassa, baryta, lime, and oxide of lead, that potassa has a stronger attraction for carbonic acid than baryta, baryta than lime, and lime than oxide of lead. The affinity of different substances for water may be determined in a similar manner.

Of all chemical substances, our knowledge of the relative degrees of attraction of acids and alkalies for each other is the most uncertain. Their mutual action is affected by so many circumstances, that it is in most cases impossible, with certainty, to refer any effect to its real cause. The only methods that have been hitherto devised for remedying this defect are those of Berthollet and Kirwan. Both are founded on the capacities of saturation, and the objections which have been urged to the rule suggested by the former philosopher apply equally to that proposed by the latter. But this uncertainty is of no great consequence in practice. We know perfectly the order of decomposition, whatever may be the actual forces by which it is effected.

SECTION II.

ON THE PROPORTIONS IN WHICH BODIES UNITE, AND ON THE LAWS OF COMBINATION.

The study of the proportions in which bodies unite naturally resolves itself into two parts. The first includes compounds whose elements appear to unite in a great many proportions; the second comprehends those, the elements of which combine in a few proportions only.

I. The compounds contained in the first division are of two kinds. In one, combination takes place unlimitedly in all proportions; in the other, it occurs in every proportion within a certain limit. The union of water with alcohol and the liquid acids, such as the sulphuric, hydrochloric, and nitric, affords instances of the first mode of combination; the solutions of salts in water are examples of the second. One drop of sulphuric acid may be diffused through a gallon of water, or a drop of water through a gallon of the acid; or they may be mixed together in any intermediate proportions; and nevertheless in each case they appear to unite perfectly with each other. A hundred grains of water, on the contrary, will dissolve any quantity of sea-salt which does not exceed forty grains. Its solvent power then ceases, because the cohesion of the solid becomes comparatively too powerful for the force of affinity. The limit to combination is in such instances owing to the cohesive power; and but for the obstacle which it occasions, the salt would most probably unite with water in every proportion.

All substances that unite in many proportions give rise to compounds which have this common character, that their elements are united by a feeble affinity, and preserve, when combined, more or less of the properties which they possess in a separate state. In a scientific point of view, these combinations are of a minor importance: but they are exceedingly useful as instruments of research. They enable the chemist to present bodies to each other, under circumstances peculiarly favourable for acting with effect: the liquid form is thus communicated to them; while the affinity of the solvent or menstruum, which holds them in solution, is not sufficiently powerful to interfere with their mutual attraction.

II. The most interesting series of compounds is produced by substances which unite in a few proportions only; and which, in combining, lose more or less completely the properties that distinguished them when separate. Of these bodies, some form but one combination. Thus there is only one compound of boron and oxygen, and of chlorine and hydrogen. Others combine in two proportions. For example, two compounds are formed by tin and oxygen, and by hydrogen and oxygen. Other bodies again unite in three, four, five, or even six proportions, which is the greatest number of compounds that any two substances are known to produce, except perhaps carbon and hydrogen, and those which belong to the first division.

The combination of substances that unite in a few proportions only, is regulated by the three following remarkable laws:—

1. The First of these Laws is, that the composition of bodies is fixed and invariable. A compound substance, so long as it retains its characteristic properties, always consists of the same elements united together in the same proportion. Sulphuric acid, for example, is always composed of sulphur and oxygen in the ratio of 16 parts of the former to 24 of the latter: no other elements can form it, nor can

it be produced by its own elements in any other proportion. Water, in like manner, is formed of 1 part of hydrogen and 8 of oxygen ; and were these elements to unite in any other ratio, some new compound, different from water, would be the product. The same observation applies to all other substances, however complicated, and at whatever period they were produced. Thus sulphate of baryta, whether formed ages ago by the hand of nature, or quite recently by the operations of the chemist, is always composed of 40 parts of sulphuric acid and 76·7 of baryta. This law, in fact, is universal and permanent. Its importance is equally manifest: it is the essential basis of chemistry, without which the science itself could have no existence.

Two views have been proposed by way of accounting for this law. The explanation now universally given is confined to a mere statement, that substances are disposed to combine in those proportions to which they are so strictly limited, in preference to any others ; it is regarded as an ultimate fact, because the phenomena are explicable on no other known principle. A different doctrine was advanced by Berthollet, in his *Statique Chimique*, published in 1803. Having observed the influence of cohesion and elasticity in modifying the action of affinity as already described, he thought he could trace the operations of the same causes in producing the effect at present under consideration. As the solubility of a salt and of a gas in water is limited, in the former by cohesion, in the latter by elasticity, he conceived that the same forces would account for the unchangeable composition of certain compounds. He maintained that within certain limits bodies have a tendency to unite in every proportion ; and that combination is never definite and invariable, except when rendered so by the operation of modifying causes, such as cohesion, insolubility, elasticity, quantity of matter, and the like. Thus, according to Berthollet, sulphate of baryta is composed of 40 parts of sulphuric acid and 76·7 of baryta, not because those substances are disposed to unite in that ratio rather than in another, but because the compound so constituted happens to have great cohesive power.

These opinions were ably and successfully combatted by Proust in several papers published in the *Journal de Physique*, wherein he proved that the metals are disposed to combine with oxygen and with sulphur only in one or two proportions, which are definite and invariable ; and a controversy ensued, remarkable for the moderation with which it was conducted on both sides. The question is now no longer at issue. The great variety of facts, similar to those observed by Proust, which have since been established, has proved beyond a doubt that the leading principle of Berthollet is erroneous. The tendency of bodies to unite in definite proportions only, is indeed so great as to excite a suspicion that all substances combine in this way; and that the exceptions thought to be afforded by this phenomena of solution, are rather apparent than real; for it is conceivable that the apparent variety of proportion, noticed in such cases, may arise from the mixture or combination of a few definite compounds with each other.

2. The Second Law of Combination is, that the relative quantities in which bodies unite, may be expressed by proportional numbers. Thus, 8 parts of oxygen united with 1 part of hydrogen, 16 of sulphur, 35·4 of chlorine, 39·6 of selenium, and 108 parts of silver. Such are the quantities of these five bodies which are disposed to unite with 8 parts of oxygen; and it is found that when they combine with one another, they unite either in the proportions expressed by those numbers, or in multiples of them according to the third law of combination. Hydrosulphuric acid, for instance, is composed of 1 part of hydrogen and 16 of sulphur, and bisulphuret of hydrogen of 1 part of hydrogen to 32 of sulphur; 35·4 of chlorine unite with 1 of hydrogen, 16 of sulphur, and 108 of silver; and 39·6 parts of selenium with 1 of hydrogen, and 16 of sulphur.

From the occurrence of such proportional numbers has arisen the use of certain terms, as *Proportion*, *Combining Proportion*, *Proportional*, and *Chemical Equivalent*, or *Equivalent*, to express them. The latter term, introduced by Wollaston, and which is employed in this treatise, was suggested by the circumstance that the combining proportion of any one body is, as it were, *equivalent* to that of another body, and may be substituted for it in combination. Among the tables at the end of the volume will be found one of the equivalents of elementary substances.

This law is not confined to elementary substances, since compound bodies have their combining proportions or equivalents, which may likewise be expressed in numbers. Thus, since water is composed of 1 eq. or 8 parts of oxygen, and 1 eq. or 1 of hydrogen, its combining proportion or equivalent is 9. The equivalent of sulphuric acid is 40, because it is a compound of one eq. or 16 parts of sulphur, and three eq. or 24 parts of oxygen; and in like manner, the eq. of hydrochloric acid is 36·4, because it is a compound of one eq. or 35·4 parts of chlorine, and one eq. or 1 part of hydrogen. The equivalent number of potassium is 39, and as that quantity combines with 8 of oxygen to form potassa, the equivalent of the latter is $39 + 8 = 47$. Now when these compounds unite, one equivalent of the one combines with one, two, three, or more equivalents of the other, precisely as the simple substances do. Hydrate of potassa, for example, is constituted of 47 parts of potassa and 9 of water, and its equivalent is consequently 47 + 9, or 56. Sulphate of potassa is composed of 40 sulphuric acid + 47 potassa; and the nitrate of that alkali of 54 nitric acid + 47 of potassa. The equivalent of the former salt is therefore 87, and of the latter 101.

The composition of the salts affords a very instructive illustration of this subject; and to exemplify it still further, a list of the equivalents of a few acids and alkaline bases is annexed:—

Hydrofluoric Acid	19·7	Lithia	14
Carbonic Acid	22	Magnesia	20·7
Hydrochloric Acid	36·4	Lime	28·5
Sulphuric Acid	40·1	Soda	31·3
Nitric Acid	54·15	Potassa	47·15
Arsenic Acid	57·7	Strontia	51·8
Selenic Acid	63·6	Baryta	76·7

The alkalies are here shown to differ widely in neutralizing power; for the equivalent of each base expresses the quantity required to neutralize an equivalent of each of the acids. Thus, 14 of lithia, 31·3 of soda, and 76·7 of baryta, combine with 54·15 of nitric acid, forming the neutral nitrates of lithia, soda, and baryta. The same fact is obvious with respect to the acids; for 40·1 of sulphuric, 54·15 of nitric, and 63·6 of selenic acid unite with 76·7 of baryta, forming a neutral sulphate, nitrate, and seleniate of baryta.

These circumstances afford a ready explanation of a curious fact, first noticed by the Saxon chemist Wenzel; namely, that when two neutral salts mutually decompose each other, the resulting compounds are likewise neutral. The cause of this fact is now obvious. If 71·3 parts of neutral sulphate of soda are mixed with 130·7 of nitrate of baryta, the 76·7 parts of baryta unite with 40 of sulphuric acid, and the 54 parts of nitric acid of the nitrate combine with the 31·3 of soda of the sulphate, not a particle of acid or alkali remaining in an uncombined condition.

Sulphate of Soda.		Nitrate of Baryta.	
Sulphuric acid	40	54	Nitric acid.
Soda	31·3	75·7	Baryta.
	71·3	130·7	

It matters not whether more or less than 71·3 parts of sulphate of soda are added; for if more, a small quantity of sulphate of soda will remain in solution; if less, nitrate of baryta will be in excess; but in either case the neutrality will be unaffected.

3. The Third Law of Combination is, that when one body, A, unites with another body, B, in two or more proportions, the quanti-

ties of the latter, united with the same quantity of the former, bear to each other a very simple ratio. The progress of chemical research, in discovering new compounds and ascertaining their exact composition, has shown that these ratios of B may be represented by one or other of the two following series :—

1st Series. A unites with 1, 2, 3, 4, 5, &c. of B.

2nd Series. A unites with 1, 1½, 2, 2½, &c. of B.

The first series is exemplified by the subjoined compounds.

Water is composed of	Hydrogen	1	Oxygen	8	1
Binoxide of Hydrogen	Do.	1	Do.	16	2
Carbonic Oxide	Carbon	6	Do.	8	1
Carbonic Acid	Do.	6	Do.	16	2
Nitrous Oxide	Nitrogen	14·15	Do.	8	1
Nitric Oxide	Do.	14·15	Do.	16	2
Hyponitrous Acid	Do.	14.15	Do.	24	3
Nitrous Acid	Do.	14·15	Do.	32	4
Nitric Acid	Do.	14·15	Do.	40	5

In all these compounds the ratio of the oxygen is expressed by whole numbers. In water the hydrogen is combined with half as much oxygen as in the binoxide of hydrogen, so that the ratio is as 1 to 2. The same relation holds in carbonic oxide and carbonic acid. The oxygen in the compounds of nitrogen and oxygen is in the ratio of 1, 2, 3, 4, and 5. In like manner the ratio of sulphur in the two sulphurets of iron, and that of chlorine in the two chlorides of mercury, is as 1 to 2. So, in bicarbonate of potassa, the alkali is united with twice as much carbonic acid as in the carbonate ; and the acid of the three oxalates of potassa is in the ratio of 1, 2, and 4.

The following compounds exemplify the second series :—

Protoxide of Iron	consists of	Iron	28	Oxygen	8	1
Peroxide		Do.	28	Do.	12	1½
Protoxide of Manganese		Manganese	27·7	Do.	8	1
Sesqui-oxide		Do.	27·7	Do.	12	1½
Bin-oxide		Do.	27·7	Do.	16	2
Arsenious Acid		Arsenic	37·7	Do.	12	1½
Arsenic Acid		Do.	37·7	Do.	20	2½
Hypophosphorous Acid		Phosphorus	15·7	Do.	4	½
Phosphorous Acid		Do.	15·7	Do.	12	1½
Phosphoric Acid		Do.	15.7	Do.	20	2½

Both of these series, which together constitute the Third Law of Combination, result naturally from the operation of the second law. The first series arises from one equivalent of a body uniting with 1, 2, 3, or more equivalents of another body. The second series is a consequence of one or two equivalents of one substance combining with 1, 3, 5, or more equivalents of another. Thus, if one or two equivalents of phosphorus unite both with 3 and with 5 equivalents of oxygen, we obtain the ratio of 1½ to 2½ ; and should one equivalent of iron combine with one of oxygen, and another compound be formed of two equivalents of iron to three of oxygen, then the oxygen united with the same weight of iron would have the ratio, as in the table, of 1 to 1½. The compounds of manganese and phosphorus with oxygen afford examples of the same nature. Still more complex arrangements will be readily conceived, such as 3 equivalents of one substance to 4, 5, or more of another. But it is remarkable that combinations of this kind are very rare; and even their existence, though theoretically possible, has not been decidedly established. Even some of the compounds which are usually included in the second series belong properly to the first. The red oxide of lead, for instance, appears in its chemical relations not so much as a direct compound of lead and oxygen, but as a kind of salt formed by the union of the binoxide of lead with the protoxide of the same metal. On this supposition the two other oxides belong to the first series.

The merit of establishing the first law of combination seems due to Wenzel, a Saxon chemist; and the second law is deducible from his experiments on the composition of the salts. His work, entitled *Lehre der Verwandtschaft*, was published in 1777. Bergmann and Richter, a few years after, confirmed the observations of Wenzel, though without adding materially in the way of generalization. Higgins in 1789 speculated on the atomic constitution of compound bodies in a manner which, if pursued, would have led to the discovery of Dalton. It is to the latter that science is indebted for deducing from the scattered facts which had been previously collected, a theory of chemical union, embracing the whole science, and giving it a consistency and form which before his time it had never possessed. In his hands the second law of combination first attained its full generality; but the discovery, which is more peculiarly his own, is that part of the third law of combination which is contained in the first of the two series above mentioned. The first public announcement of his views appears to have been made to the Philosophical Society of Manchester in 1803; and in 1808 they were explained in his New System of Chemical Philosophy. In the same year Wollaston and Thomson gave their evidence in support of the new doctrine, and other chemists have followed in the same path of inquiry. But of all who have successfully laboured in establishing the laws of combination, the most splendid contribution is that of the celebrated Berzelius. Struck with the perusal of the works of Richter, he commenced in 1807 an investigation into the Laws of Definite Proportion. Since that period his labours in this important field have been incessant, and every department of the science has been enriched by his skill and indefatigable industry. Whether we look to pneumatic chemistry, to the chemical history of the metals and of the salts, or to the composition of minerals, we are alike indebted to Berzelius. In all has he traced the laws of definite proportion, and by a multitude of exact analyses given to the laws of combination that certainty which accumulated facts can alone convey.

The utility of being acquainted with these important laws is manifest. Through their aid, and by remembering the equivalents of a few elementary substances, the composition of an extensive range of compound bodies may be calculated with facility. Thus by knowing that 6 is the eq. of carbon and 8 of oxygen, it is easy to recollect the composition of carbonic oxide and carbonic acid; the first consisting of 6 parts of carbon + 8 of oxygen, and the second of 6 carbon + 16 of oxygen. The eq. of potassium is 39; and potassa, its protoxide, is composed of 39 of potassium + 8 of oxygen. From these few data, the composition of carbonate and bicarbonate of potassa are given; the former being composed of 22 parts of carbonic acid + 47 potassa, and the latter of 44 carbonic acid + 47 potassa. This method acts as an artificial memory, the advantage of which, compared with the former practice of stating the composition in 100 parts, will be manifest by inspecting the following quantities, and attempting to recollect them.

	Carbonic Oxide.	Carbonic Acid.
Carbon	42·86	27·27
Oxygen	57·14	72·73

	Carbonate of Potassa.	Bi-carbonate of Potassa.
Carbonic acid	31·43	47·83
Potassa	68·57	52·17

From the same data, calculations, which would otherwise be difficult or tedious, may be made rapidly and with ease, without reference to books, and frequently by a simple mental process. The exact quantities of substances required to produce a given effect may be determined with certainty, thus affording information which is often necessary to the success of chemical processes, and of great consequence both in the practice of the chemical arts, and in the operations of pharmacy.

The same knowledge affords a good test to the analyst by which he may judge of the accuracy of his result, and even sometimes correct an analysis which he has not the means of performing with rigid precision. Thus a powerful argument for the accuracy of an analysis is derived from the correspondence of its result with the laws of chemical union. On the contrary, if it form an exception to them, we are authorized to regard it as doubtful; and may hence be led to detect an error, the existence of which might not otherwise have been suspected. If an oxidized body be found to contain one equivalent of the combustible with 7·99 of oxygen, it is fair to infer that 8, or one equivalent of oxygen, would have been the result, had the analysis been perfect.

The composition of a substance may sometimes be determined by a calculation, founded on the laws of chemical union, before analysis of it has been accomplished. When the new alkali lithia was first discovered, chemists did not possess it in sufficient quantity for determining its constitution analytically. But the neutral sulphates of the alkalies and alkaline earths are known to be composed of one equivalent of each constituent, and the oxides to contain one eq. of oxygen. If it be found, therefore, by analysis, that neutral sulphate of lithia is composed of 40 parts of sulphuric acid and 14 of lithia, it may be inferred, since 40 is one eq. of the acid, that 14 is the eq. for lithia; and that this oxide is formed of 8 parts of oxygen and 6 of lithium.

The method of determining equivalent numbers will be anticipated from what has already been said. The commencement is made by carefully analyzing a definite compound of two simple substances which possess an extensive range of affinity. Thus water, a compound of oxygen and hydrogen, is found to contain 8 parts of the former to 1 of the latter; and if it be assumed that water consists of 1 eq. of oxygen and 1 of hydrogen, the relative weights of these equivalents will be as 8 to 1. The chemist then selects for analysis such compounds as he believes to contain 1 eq. of each element, in which either oxygen or hydrogen, but not both, is present. Carbonic oxide and hydro-sulphuric acid are suited to his purpose: as the former consists of 8 parts of oxygen and 6 of carbon, and the latter of 1 part of hydrogen and 16 of sulphur, the equivalent of carbon is inferred to be 6, and that of sulphur 16. The equivalent of all the other elements may be determined in a similar manner.

In researches on chemical equivalents there are two kinds of difficulty, one involved in the processes for ascertaining the exact composition of compounds, and the other in the selection of the compounds which contain single equivalents. Important general precautions in the experimental part of the subject are the following:—1, to exert scrupulous care about the purity of materials; 2, to select methods which consist of a few simple operations only; 3, to repeat experiments, and with materials prepared at different times; 4, to arrive at the same conclusion by two or more processes independent of each other. In the selection of compounds of single equivalents there are several circumstances calculated to direct the judgment:—

1. If two substances combine in several proportions, the law of multiples usually effects the electro-negative element of a compound. Thus, in the 5 compounds of nitrogen and oxygen, in which oxygen is the — element, 14 parts of nitrogen are united with 8, 16, 24, 32, and 40 parts of oxygen; whereas, taking the quantity of oxygen as constant, 8 parts of oxygen are united with 14, 7, 4·66, 3·5, and 2·8 parts of nitrogen, in which the simple ratio of the first series does not exist. This circumstance induces the chemist always to search among the oxides of the same element for the lowest grade of oxidation, and in most cases to consider it as a compound of single equivalents. In some instances, however, the second degree of oxidation is formed of single equivalents, while the lowest oxide consists of 2 eq. of the + element and one of oxygen. Such compounds are called *dinoxides* and sometimes *suboxides*.

2. Metallic oxides, distinguished for strong alkalinity, or for acting as strong alkaline bases, are always protoxides. Dinoxides rarely unite definitely with acids, and are remarkable for their ready conversion into protoxides with separation of metal. If the same metal yield several oxides, the protoxide is the strongest base; the highest grade of oxidation is frequently an acid, and the intermediate oxides are in general little distinguished either for alkalinity or acidity. Protoxides usually resist decomposition more obstinately than other oxides.

3. When a metal forms two oxides, the oxygen of which is in the ratio of 1 to 1½, the first is usually the protoxide, and the second a compound of 2 eq. of the metal to 3 of oxygen. The oxides of iron and nickel are examples.

4. If two compounds resemble each other in their modes of combination, it is a strong presumption that their constitution is similar. Alumina and the peroxide of iron are remarkably allied in their chemical relations; and hence it is inferred, since the latter consists of 2 eq. of iron and 3 eq. of oxygen, that the former, whose composition would otherwise be very doubtful, is composed of 2 eq. of aluminium and 3 eq. of oxygen.

5. Mitscherlich has found, as is more fully stated in the article on crystallization, that certain compounds which resemble each other in composition and in their modes of combining, are likewise disposed in crystallizing to affect the same form. Hence it is a strong presumption that compounds which are analogous both in their crystalline figure and modes of combining, are also similar in their composition. In the oxide and acid of chromium the oxygen is in the ratio 1 to 2, and hence it was first supposed that 1. eq. of chromium was united in

the oxide with 1 eq. and in the acid with 2 eq. of oxygen. But the chromates resemble the sulphates in form and modes of combining, and the oxide of chromium bears the same analogy to alumina and peroxide of iron. The inference is, that oxide of chromium consists of 2 eq. of chromium and 3 eq. of oxygen, and chromic acid of 1 eq. of chromium and 3 eq. of oxygen.

6. Another guide in these inquiries is derived from the relation traced by Dulong and Petit between the equivalents of a body and its sp. heat. The coincidences pointed out at page 34 are sufficiently numerous to show an interesting relation which is sometimes useful in selecting between doubtful numbers; but the instances of failure are at present too frequent to admit of this principle being used except with much caution.

7. The ready decomposition by galvanism, observed by Faraday, of compounds which consist of single equivalents, and the resistance to the same agent of many others not so constituted, promises to become an indication of great value in determining eq. numbers. The facts as yet known respecting it will be found in the section on galvanism.

8. Great light is often thrown on the chemical constitution of a compound by a knowledge of the *volumes* of the substances of which it is composed. This subject, however, will be discussed in an after part of this section.

Since the equivalents merely express the relative quantities of different substances which combine together, it is in itself immaterial what figures combine to express them. The only essential point is, that the relation should be strictly observed. Thus, the eq. of hydrogen may be assumed as 10; but then oxygen must be 80, carbon 60, and sulphur 160. We may call hydrogen 100 or 1000; or if it were desirable to perplex the subject as much as possible, some high uneven number might be selected, provided the due relation between the different numbers were faithfully preserved. But such a practice would destroy the advantage above described to the use of equivalents; and it is the object of every one to employ such as are simple, that their relation may be perceived by mere inspection. Thomson makes oxygen 1, so that hydrogen is eight times less than unity, or 0·125, carbon 0.75, and sulphur 2. Wollaston, in his scale of chemical equivalents, estimated oxygen at 10; and hence hydrogen is 1·25, carbon 7·5, and so on. According to Berzelius, oxygen is 100. And lastly, several other chemists, such as Dalton, Davy, Henry, and others, selected hydrogen as their unit; and therefore the eq. of oxygen is 8. One of these series may easily be reduced to either of the others by an obvious and simple calculation. The numbers adopted in this work refer to hydrogen as unity, and are given in a table (Appendix in Table I.) constructed principally from the published tables of Berzelius, and partly from facts supplied by my own researches. The hypothesis that all equivalent numbers are simple multiples of the eq. of hydrogen, has been elsewhere shown to be untenable. (Phil. Trans. 1833, Part ii. page 523.) Whenever the experimental quantity is nearly a whole number, the last may for many purposes be used as a sufficient approximation; and, accordingly, for such elements as carbon, sulphur, nitrogen, and potassium, which are often referred to in the way of illustration, I have generally adopted round numbers, as being shorter and more easily remembered than fractions. But on all occasions where exact calculations are concerned, the numbers given in the table should be employed.

The useful instrument known by the name of the *Scale of Chemical Equivalents*, was devised by Wollaston, and is a table of equivalents comprehending all those substances which are most frequently employed by chemists in the laboratory; and it only differs from other tabular arrangements of the same kind, in the numbers being attached to a sliding rule, which is divided according to the principle of that of Gunter. From the mathematical construction of the scale, it not only serves the same purpose as other tables of equivalents, but in many instances supersedes the necessity of calculation. Thus, by inspecting the common table of equivalents we learn that 87 parts, or 1 eq. of sulphate of potassa, contain 40 parts of sulphuric acid and 47 of potassa: but recourse must be had to calculation, when it is wished to determine the quantity of acid or alkali in any other quantity of the salt. This knowledge, on the contrary, is obtained directly by means of the scale of chemical equivalents. For example, on pushing up the slide until 100 marked upon it is in a line with the name sulphate of potassa on the fixed part of the scale, the numbers opposite to the terms sulphuric acid and potassa will give the precise quantity of each contained in 100 parts of the compound. In the original scale of Wollaston, for a particular account of which I may refer to the Philosophical Transactions for 1814, oxygen is taken as the standard of comparison; but hydrogen may be selected for that purpose with equal propriety, and scales of this kind have been prepared for sale by Reid of Edinburgh. A very complete scale of equivalents has been drawn up by Prideaux of Plymouth. (Phil. Mag. and Annals, viii. 430.)

ON THE ATOMIC THEORY.

The brief sketch which has been given of the laws of combination will, I trust, set in its true light the importance of that department of chemical science. It is founded on experiment alone, and the laws which have been stated are the mere expression of fact. It is not necessarily connected with any speculation, and may be kept wholly free from it. The notion that the laws of combination involve something uncertain or hypothetical, is a fallacy easily referable to its source. It was impossible to reflect on the regularity and constancy with which bodies obey these laws, without speculating about the cause of that regularity; and, consequently, the facts themselves were no sooner noticed, than an attempt was made to explain them. Accordingly, when Dalton published his discovery of those laws, he at once incorporated the description of them with his notion of their physical cause, and even expressed the former in language suggested by the latter. Since that period, though several British chemists of eminence, and in particular Wollaston and Davy, recommended and practised an opposite course, both subjects have been too commonly comprised under the name of *atomic theory;* hence it has often happened that beginners have rejected the whole as hypothetical, because they could not satisfactorily distinguish those parts which are founded on fact from those which are conjectural. All such perplexity would have been avoided, and this department of the science have been far better understood, and its value more justly appreciated, had the discussion concerning the atomic constitution of bodies been always kept distinct from that of the phenomena which it is intended to explain. When employed in this limited sense, the atomic theory may be discussed in a few words.

Two opposite opinions have long existed concerning the ultimate elements of matter. It is supposed, according to one party, that every particle of matter, however small, may be divided into smaller portions, provided our instruments and organs were adapted to the operation. Their opponents contend, on the other hand, that matter is composed of certain ultimate particles or molecules, which by their nature are indivisible, and are hence termed *atoms* (from *α not,* and *τεμνειν to cut*). These opposite opinions have from time to time been keenly contested, and with variable success, according to the acuteness and ingenuity of their respective champions. But it was at last perceived that no positive data existed capable of deciding the question, and its interest therefore gradually declined. The progress of modern chemistry has revived attention to this controversy, by affording a far stronger argument in favour of the atomic constitution of matter than was ever advanced before, and one which is almost irresistible. For the assumption that all bodies consist of ultimate atoms, the weight of which differs in different kinds of matter, supplies a luminous explanation of the laws of chemical union, which do not appear explicable on any other supposition.

According to the atomic theory, every compound is formed of the atoms of its constituents. An atom of A may unite with 1, 2, 3, or more atoms of B. Thus, supposing water to be composed of 1 atom of hydrogen and 1 atom of oxygen, binoxide of hydrogen will consist of 1 atom of hydrogen and 2 atoms of oxygen. If carbonic oxide is formed of 1 atom of carbon and 1 atom of oxygen, carbonic acid will consist of 1 atom of carbon and 2 atoms of oxygen. If, in the compounds of nitrogen and oxygen, enumerated at page 150, the first or protoxide consist of 1 atom of nitrogen and 1 atom of oxygen, the four others will be regarded as compounds of 1 atom of nitrogen to 2, 3, 4, and 5 atoms of oxygen. From these instances it will appear that the law of multiple proportion is a necessary consequence of the atomic theory. There is also no apparent reason why 1, 2, or more atoms of 1 substance may not combine with 2, 3, 4, 5, or more atoms of another; but, on the contrary, these arrangements are necessary in explanation of the not unfrequent occurrence of half equivalents, as formerly stated. Such combinations will also account for the complicated proportions noticed in certain compounds, especially in many of those belonging to the animal and vegetable kingdoms.

In consequence of the satisfactory explanation which the laws of chemical union receive by means of the atomic theory, it has become customary to employ the term *atom* in the same sense as combining proportion or equivalent. For example, instead of describing water as a compound of 1 eq. of oxygen and 1 eq. of hydrogen, it is said to consist of 1 atom of each element. In like manner sulphate of potassa is said to be formed of 1 atom of sulphuric acid and 1 atom of potassa, the word in this case denoting as it were a compound atom, that is, the smallest integral particle of the acid or alkali; a particle which does not admit of being divided, except by the separation of its elementary or constituent atoms. The numbers expressing the proportions in which bodies unite must likewise indicate, consistently with this view, the relative weights of atoms; and accordingly these numbers are often called *atomic weights.* Thus, as water is composed of 8 parts of oxygen and 1 of hydrogen, it follows, on the supposition of water consisting of 1 atom of each element, that an atom of oxygen must be 8 times heavier than an atom of hydrogen. If carbonic oxide be formed of an atom of carbon and an atom of oxygen, the relative weights of their atoms are as 6 to 8 ; and in short the chemical equivalents of all bodies may be considered as expressing the relative weights of their atoms.

The foregoing argument in favour of the atomic constitution of matter becomes much stronger when we trace the intimate connection which subsists among many substances, between their crystalline form and chemical composition. This subject, however, now known under the name of *isomorphism*, will be more conveniently discussed under the head of crystallization.

Dalton supposes the atoms of bodies to be spherical ; and he has invented certain symbols to represent the mode in which he conceives they may combine together, as illustrated by the following figures :—

⊙ Hydrogen. ○ Oxygen.
⦶ Nitrogen. ● Carbon.

BINARY COMPOUNDS.

○⊙ Water.
○● Carbonic oxide.

TERNARY COMPOUNDS.

○⊙○ Binoxide of hydrogen.
⊙●○ Carbonic acid.
&c. &c. &c.

All substances containing only 2 atoms he called binary compounds, those composed of 3 atoms ternary, those composed of 4 quaternary, and so on.

There are several questions relative to the nature of atoms, most of which will perhaps never be decided. Of this nature are the questions which relate to the actual form, size, and weight of atoms, and to the circumstances in which they mutually differ. All that we know with any certainty is, that their weights do differ, and by exact analysis the relations between them may be determined. Peculiar views of the constitution of matter are held by Ampère, whose opinions are always acute and philosophical. He not only believes dissimilar atoms, as of oxygen and hydrogen, to be capable of uniting, but that 2 or more atoms of the same kind have a power of mutual attraction whereby they are arranged in groups of definite figure, which he calls *molecules.* These molecules, more or less intimately bound together by cohesion, give rise to the different states of bodies, the solid, liquid, and gaseous. Thus, oxygen gas is conceived not an assemblage of self-repulsive atoms of oxygen, but of molecules, each of which is a polyhedral solid made up of a constant number of atoms and repulsive to neighbouring molecules. In like manner he conceives the ultimate particles of compounds, as water and potassa, to be arranged in groups so as to constitute molecules. Similar views are maintained by Prout in his Bridgewater Treatise. This doctrine receives strong support from some phenomena of gaseous combination, and from the complex nature of organic compounds.

It is but justice to the memory of Higgins, to state that he first made use of the atomic hypothesis in chemical reasonings. In his "Comparative View of the Phlogistic and Antiphlogistic Theories," published in the year 1789, he observes (pages 36 and 37) that "in volatile vitriolic acid a single ultimate particle of sulphur is intimately united only to a single particle of dephlogisticated air; and that, in perfect vitriolic acid, every single particle of sulphur is united to 2 of dephlogisticated air, being the quantity necessary to saturation;" and he reasons in the same way concerning the constitution of water and the compounds of nitrogen and oxygen. These remarks of Higgins do not appear to have had the slightest connection with the subsequent views of Dalton, who seems to have never seen the work of Higgins till after he had given an account of his own doctrine. The observations of Higgins, though highly creditable to his sagacity, do not affect Dalton's merit as an original observer. They were made, moreover, in so casual a manner, as not only not to have attracted the notice of his contemporaries, but to prove that Higgins himself attached no particular interest to them. Dalton's chief merit consists in having formed a complete theory of chemical union, and in the discovery of an essential and most important part of the doctrine, a merit which is solely and indisputably his; but in which he would have been anticipated by Higgins, had that chemist perceived the importance of his own opinions.

To the student who may desire a more ample account of the doctrine of atoms than the nature and limits of this volume admit of being given here, I may recommend a small work by Daubeny on the atomic theory, which in other respects will be found well worthy of perusal.

ON THE THEORY OF VOLUMES.

Soon after the publication of the New System of Chemical Philosophy in 1808, in which work Dalton explained his views of the atomic constitution of bodies, Gay-Lussac published in the *Memoires d'Arcueil* on the "Combination of Gaseous Substances with one another." He there proved that gases unite together by volume in very simple proportions, which he exemplified by the ratios in which the following gases unite :—

100 Hydrogen	to	50 Oxygen.
100 Ammoniacal		100 Hydrochloric Acid Gas.
100 do.		100 Fluoboric Acid Gas.
100 do.		200 do.
100 do.		100 Carbonic Acid Gas.
100 do.		200 do.

Various other examples were quoted, both from his own experiments and from those of others, all demonstrating the same fact. Thus, ammonia was found by A. Berthollet to consist of 100 volumes of nitrogen gas and 300 volumes of hydrogen ; sulphuric acid contains 100 volumes of sulphurous acid and 50 volumes of oxygen ; and carbonic acid is formed by burning a mixture of 50 volumes of oxygen and 100 volumes of carbonic oxide.

From these and other instances Gay-Lussac established the fact, that gaseous substances unite in the simple ratio of 1 to 1, 1 to 2, 1 to 3, &c.; and this original observation has been confirmed by such a multiplicity of experiments, that it may be regarded as one of the best established laws in chemistry. Nor does it apply to gases merely, but to vapours also. For example, hydrosulphuric, sulphurous, and hydriodic acid gases are composed of

600 vol. hydrogen gas and	100 vol. vapour of	sulphur.
600 oxygen	100	sulphur.
100 hydrogen	100	iodine.

Another remarkable fact established by Gay-Lussac in the same essay is, that the volumes of compound gases and vapours always bear a very simple ratio to the volumes of their elements. This will appear from the following table, in which all the substances are supposed to be in the gaseous state :—

Volumes of Elements.				Volumes of resulting Compounds.
100 Nitrogen	+	300 Hydrogen	yield	200 Ammonia.
50 Oxygen	+	100 Hydrogen		100 Water.
50 Oxygen	+	100 Nitrogen		100 Protoxide of Nitrogen.
100 Sulphur	+	600 Hydrogen		600 Hydrosulphuric Acid.
100 Sulphur	+	600 Oxygen		600 Sulphurous Acid.
100 Chlorine	+	100 Hydrogen		200 Hydrochloric Acid.
100 Iodine	+	100 Hydrogen		200 Hydriodic Acid.
100 Bromine	+	100 Hydrogen		200 Hydrobromic Acid.
100 Cyanogen	+	100 Hydrogen		200 Hydrocyanic Acid.
100 Oxygen	+	100 Nitrogen		200 Binoxide of Nitrogen.

The law of multiples is equally demonstrable by means of combining or eq. volumes as by combining or eq. weights. The following tabular view will justify this statement.

Volumes of Elements.				Resulting Compounds.
100 Nitrogen	+	50 Oxygen	yield	Protoxide of Nitrogen.
100 do.	+	100 do.	. . .	Binoxide of Nitrogen.
100 do.	+	150 do.	. . .	Hyponitrous Acid.
100 do.	+	200 do.	. . .	Nitrous Acid.
100 do.	+	250 do.	. . .	Nitric Acid.
100 Hydrogen	+	50 do.	. . .	Water.
100 do.	+	100 do.	. . .	Binoxide of Hydrogen.
100 Carbon vapour	+	50 do.	. . .	Carbonic Oxide.
100 do.	+	100 do.	. . .	Carbonic Acid.

It thus appears that the laws of combination may equally well be deduced from the volumes as from the weights of the combining substances, and that the composition of gaseous bodies may be expressed as well by measure as weight. In the subjoined table is a comparative view of equivalent weights and volumes, to which is added the respective sp. gravities in relation both to air and hydrogen : the facts respecting the vapours are drawn from an essay by Mitscherlich. (An. de Ch. et Ph. lv. 5.) In constructing the table 100 volumes of hydrogen are assumed as the unit to which the eq. vol. of other substances are compared, and as the volume occupied by a weight of hydrogen represented by its equivalent. The eq. vol. of other substances, considered as gases, are in like manner the volumes corresponding to their equivalents taken as weights. In all substances whose sp. gr. and equivalents are the same compared to the sp. gr. and eq. of hydrogen as unity, the eq. vol. is 100. If the sp. gr. is smaller than its equivalent, as in mercury, this must arise from its eq. vol. being proportionally greater than the eq. vol. of hydrogen ; and if the sp. gr. is greater than its equivalent, as in oxygen or sulphur, the eq. vol. is proportionally smaller than the eq. vol. of hydrogen. A simple rule of three, therefore, enables the eq. vol. to be calculated. Thus, the eq. vol. of mercury is $\frac{202}{101} \times 100 = 200$; that of oxygen $\frac{8}{16} \times 100 = 50$; and that of sulphur is $\frac{16{\cdot}10}{96{\cdot}48} \times 100 = 16{\cdot}66$, agreeably to the numbers which will be found in the table.

Gas and Vapours.	Specific Gravities.		Chemical Equivalents.	
	Air as 1.	Hydrogen as 1.	By Vol.	By Weight.
Hydrogen	0·0690	1·00	100	1·00
Nitrogen . . .	0·9727	14·12	100	14·15
Chlorine	2·4700	35·84	100	35·42
Carbon (hypothetical) . .	0·4215	6·12	100	6·12
Iodine	8·7011	126·30	100	126·30
Bromine . . .	5·3930	78·40	100	78·40
Water	0·6202	9·00	100	9·00
Alcohol	1·6012	23·24	100	23·25
Sulphuric Ether . . .	2·5822	37·50	100	37·50
Light Carburretted Hydrogen .	0·5595	8·12	100	8·12

Gas and Vapours.	Specific Gravities.		Chemical Equivalents.	
	Air as 1.	Hydrogen as 1.	By Vol.	By Weight.
Olefiant Gas	0·9810	14·24	100	14·24
Carbonic Oxide	0·9727	14·12	100	14·12
Carbonic Acid	1·5239	22·12	100	22·12
Protoxide of Nitrogen	1·5239	22·12	100	22·15
Sulphurous Acid	2·2105	32·10	100	32·10
Sulphuric Acid (anhydrous)	2·7617	40·10	100	40·10
Cyanogen	1·8157	26·35	100	26·35
Hydrosulphuric Acid	1·1770	17·10	100	17·10
Binoxide of Nitrogen	1·0377	15·06	200	30·15
Mercury	6·9690	101·00	200	202·00
Ammonia	0·5898	8·56	200	17·15
Hydrochloric Acid	1·2695	18·42	200	36·42
Hydriodic Acid	4·3850	63·63	200	127·26
Hydrobromic Acid	2·7310	39·71	200	79·40
Hydrocyanic Acid	0·9423	13·67	200	27·35
Arsenuretted Hydrogen	2·6950	39.20	200	78·20
Sesquichloride of Arsenic	6·2950	91·36	200	181·66
Sesquiodide of Arsenic	15·6400	227·00	200	454·28
Protochloride of Mercury	8·2040	119·00	200	237·42
Bichloride of Mercury	9·4390	137·00	200	272·84
Bromide of Mercury	9·6650	140·26	200	280·40
Bibromide of Mercury	12·3620	179·40	200	358·80
Biniodide of Mercury	15·6700	227·40	200	454·52
Oxygen	1·1025	16·00	50	8·00
Arsenious Acid	13·6695	198·40	50	99·40
Phosphorus	4·3273	62·80	50	31·4
Arsenic	10·3620	150·80	50	74·4
Sulphur	6·6480	96·48	16·66	16·10
Bisulphuret of Mercury	5·3840	78·10	33·33	234·18

The observations which more immediately flow from the facts in the preceding table are these :—

1. The combining or eq. volumes of substances, both elementary and compound, are either equal or have the simple ratio of 1 to 1, 1 to 2, 1 to 3, &c. The same simplicity rarely exists among the equivalent weights.

2. On comparing together the third and fifth columns, the corresponding numbers for the first eighteen substances will be found nearly or quite identical. As those substances have the same uniting volume as hydrogen, which is the assumed unit of comparison, and as the sp. gravities are merely the weights of equal volumes, the numbers of the third column, were they quite exact, must coincide with those in the fifth : their want of identity indicates errors of observation.

3. The identity in the eq. volumes of the elementary gases, hydrogen, nitrogen, and chlorine, led to the notion that the eq. volumes of most other elements, such as carbon, sulphur, and phosphorus, might also be identical. Assuming that identity, the sp. gravity which those

elements ought to have when gaseous may easily be calculated. Thus, taking 1, 6·12, and 16·1 as the equivalents of hydrogen, carbon, and sulphur, then will their sp. gravities in the gaseous state, eq. volumes being supposed equal, be in the ratio of 1, 6·12, and 16·1. This method, by which the hypothetical sp. gravity of carbon, as stated in the table, was obtained, was first indicated by Dr. Prout. (An. of Phil. vi. 321.) But though such hypothetical numbers may sometimes be used for the convenience of expressing the relation of uniting substances by measure, recent facts show how dangerous it would be to confide in them; for by the table it appears that the eq. volume of sulphurous vapour is one-sixth of that of hydrogen, which renders the sp. gravity of the vapour of sulphur six times greater that the hypothetical number. Similar deviation is observable in phosphorus, arsenic, and mercury. In these cases, the real sp. gravity of a vapour is as much greater or less than the hypothetical as its eq. volume is less or greater than that of hydrogen.

4. The identity in the eq. volumes of hydrogen, nitrogen, and chlorine suggested the idea that the atoms of all the elements are of the same magnitude; and this, coupled with the supposition that the self-repulsive energy of these atoms is equal, led to the opinion that equal volumes of the elements in the gaseous state must contain an equal number of atoms. This hypothesis, recommended by its simplicity, and supported by the fact that the volumes of gaseous substances vary according to the same law by varying temperature and pressure, was accordingly employed as a mode of determining the relative weights of atoms. As water consists of 50 measures of oxygen and 100 of hydrogen gas, it was inferred to be a compound of one atom of oxygen and two atoms of hydrogen; and consequently, taking 8 as the weight of an atom of oxygen, the weight of one atom of hydrogen is $\frac{1}{2}$ instead of 1, as in the table; or taking hydrogen as 1, the atom of oxygen is 16. On the same principle may the numbers which in the table represent the eq. weights of chlorine, bromine, iodine, and nitrogen, which have the same eq. volumes as hydrogen, be considered as the weights of two equivalents. The equivalents adopted by Davy in his Elements of Chemical Philosophy, as well as those of Berzelius, which are now in general use on the Continent, were framed in accordance with these views: this British chemists ought to bear in mind, since the same numbers which Berzelius uses for 2 eq. of hydrogen, nitrogen, chlorine, bromine, and iodine, they consider as one equivalent. But the opinion of Davy and Berzelius must now either be abandoned, or maintained on other principles, since the late researches of Dumas and Mitscherlich have shewn experimentally that

eq. volumes of the elementary gases and vapours do not contain the same number of atoms.

5. The facts contained in the last and preceding tables supply material for calculating the sp. gravity of compound gases, by which means the accuracy of other conclusions respecting their composition may be verified. Thus analysis proves that ammoniacal gas is composed of 100 volumes of nitrogen and 300 of hydrogen gases, condensed into the space of 200 volumes: if so, its sp. gravity will be

$$\frac{0{\cdot}9727 + 3 \times 0{\cdot}069}{2} = \frac{1{\cdot}1797}{2} = 0{\cdot}5889.$$

The near agreement of this calculated number with that found by weighing the gas itself, proves that ammonia has really the constitution above assigned to it, and gives great probability that the sp. gravity of nitrogen and hydrogen gases is nearly correct.

Again, hydrochloric acid gas consists of 100 volumes of hydrogen and 100 of chlorine gases, united without any change of bulk. Hence its sp. gr. ought to be

$$\frac{2{\cdot}47+0{\cdot}069}{2} = 1{\cdot}2695.$$

Hydrocyanic acid vapour is formed of 100 volumes of hydrogen and 100 of cyanogen gases, united without change of volume; and therefore its sp. gravity should be

$$\frac{1{\cdot}8157+0{\cdot}069}{2} = 0{\cdot}9423.$$

Considering olefiant gas as a compound of 200 volumes of hydrogen gas and 200 of the vapour of carbon condensed into 100, its sp. gravity will be $2 \times 0{\cdot}069 + 2 \times 0{\cdot}4215 = 0{\cdot}1380 + 0{\cdot}8430 = 0{\cdot}9810$.

Aqueous vapour is composed of 100 volumes of hydrogen and 50 of oxygen gases, condensed into the space of 100 volumes; and therefore its sp. gravity ought to be $0{\cdot}069 + 0{\cdot}5512$ (half the sp. gr. of oxygen) $= 0{\cdot}6202$.

Protoxide of nitrogen is formed of 100 volumes of nitrogen and 50 of oxygen gases, condensed into 100 volumes; and hence its sp. gravity should be $0{\cdot}9727 + 0{\cdot}5512 = 1{\cdot}5239$.

Assuming carbonic oxide to be a compound of 100 volumes of carbon vapour, and 50 of oxygen gas, contracted in uniting into 100 volumes, its sp. gravity should be $0{\cdot}4215 + 0{\cdot}5512 = 0{\cdot}9727$.

As the different sp. gravities thus calculated are very nearly those found by direct experiment, there is a strong presumption that the elements of the calculations are correct.

The principle of these calculations is sufficiently obvious. The sp. gravities represent the weights of equal volumes of the gases; taking 100 as the standard volume of which the sp. gravity of each gas denotes the weight, then 50 volumes of a gas may be indicated by half, 25 volumes by a fourth, and 16·66 by a sixth of its sp. gravity. Thus, hydrosulphuric acid is a compound of 100 volumes of hydrogen gas, and 16·66 ($\frac{100}{6}$) of the vapour of sulphur, condensed into 100 volumes, and therefore its sp. gravity is

$$0{\cdot}069 + \frac{6{\cdot}6480}{6} = 0{\cdot}069 + 1{\cdot}1080 = 1{\cdot}1770.$$

Sulphurous acid consists of 100 volumes of oxygen gas and 16·66 of the vapour of sulphur, condensed into 100 volumes; and hence its sp. gravity is

$$1{\cdot}1025 + \frac{6{\cdot}6480}{6} = 1{\cdot}1025 + 1{\cdot}1080 = 2{\cdot}2105.$$

In these two gases the volume is the same as the hydrogen or oxygen which they contain, and therefore their sp. gravities are the sum of the weights of their elements. The same applies to water, protoxide of nitrogen, and carbonic oxide. In olefiant gas 400 volumes are condensed into 100, and therefore its sp. gravity is the sum of the sp. gravities of its elements. Hydrochloric acid gas occupies the same space as its elements, and therefore its sp. gravity is found by taking the mean of their sp. gravities. The same remark applies to hydrocyanic acid. In ammonia 400 volumes are condensed into 200, and therefore the sum of the sp. gravities is halved.

As vapours are easily condensed by cold, and in many cases exist as such only at high temperatures, their sp. gravities may often be obtained by calculation more accurately than by experiment. Thus, it is easier accurately to ascertain the sp. gravity of hydrogen and hydrosulphuric acid gases than of the vapour of sulphur; and therefore, as soon as experiment has shewn that the sp. gravity of that vapour is *somewhere about* 6·6480, then the precise number may be calculated. For, as 100 volumes of hydrosulphuric acid gas contain 100 of hydrogen gas, the sp. gravity of the latter deducted from that of the former (1·177 – 0·069) gives 1·108 as the weight of combined sulphur. If the eq. volume of sulphur were 100, then must 1·108 be its sp. gravity; but, as the number found experimentally is nearly six times 1·108, the inference is that the real sp. gravity is 6 × 1·108 = 6·648, and that its eq. volume is six times less than 100, or 16·66. The only assumption here is, that, if the eq. volume of the vapour is not 100, it must be some multiple or sub-multiple of it by a whole number, consistently with the *theory of volumes.* In the construction of the preceding table, I have given the sp. gravities of vapours calculated on these principles, rather than the precise numbers given by experiment.

6. The volume of a compound gas in reference to the volumes of its components is determined by one of the following rules :—

i. One volume of gas united with one volume yields two volumes of the compound.

ii. The volume of the compound gas often has the volume of that gas which enters most largely into it by volume.

iii. The volume of the compound gas is equal to the sum of the volumes of its components divided generally by 2, but sometimes by 4 or 8.

iv. In a few cases the sum of the component volumes must be divided by 3.

ON ATOMIC OR EQUIVALENT VOLUMES.

The preceding section shows that the relation between the equivalents of elementary bodies and their volumes in the gaseous form is a very simple one. It now becomes a question, what is the relation between the equivalents of such bodies and their volumes in the solid or liquid forms?

Assuming that matter is formed of atoms, differing in weight in different elements, two views may be entertained. According to one, all atoms have the same specific gravity; and therefore, if the atom of one element be twice as heavy as that of another, it must be also twice as large. According to the other, the atoms of different elements are supposed to differ in weight, even when supposed to have the same absolute size. The general opinion of chemists seems to be in favour of the former view.

On that view it is obvious, that the more atoms are contained in a given volume, and the heavier these atoms are, the greater must be the specific gravity or density of the substance. Hence, the density must be the product of the atomic weight multiplied into the number of atoms in an equal volume. But the density being known, as well as the atomic weight, then the density, divided by the atomic weight or equivalent, must give the number of atoms in an equal volume.

Referring to the table, p. 163, it is evident that the densities of the elementary bodies in the first division, divided by the atomic or equivalent weights, must give the quotient 1; those in the second division will give 0·5; and those in the third will give, for oxygen 2, for phosphorus and arsenic 4, and for sulphur 6; and that these numbers will represent the relative numbers of atoms in equal volumes. We see also, by that table, that in bodies where the number of atoms in equal volumes is the same, as in the case of the bodies of the first division, the density in the gaseous form and atomic weight must coincide, hydrogen being employed as the standard of comparison for both. We see, further, that what has been called the equivalent volume in the gaseous state is inversely as the number of atoms in equal volumes.

In the case of solid and liquid bodies the relation is not so simple, because, from various disturbing causes, such as the relative force of cohesion, &c., they differ enormously in the number of atoms contained in equal volumes.

If we divide the densities, in the solid or liquid state, by the atomic weights, we obtain the relative numbers of atoms in equal volumes; and by dividing the atomic weights by the densities, we obtain what are called the *atomic volumes* (Kopp), more properly *equivalent volumes* (Schrœder). As before, in the case of gaseous bodies, so now, in that of solids and liquids, the atomic volume is inversely as the number of atoms in equal volumes.

In the following table are contained a few examples to illustrate what is meant.

Element.	Equivalent.	Density.	Number of Atoms in equal Volumes.	Atomic Volumes.
Carbon . .	6	3·5 (Diamond)	·5833	1·714
Sulphur .	16	2·0 . .	·1250	8·000
Potassium . .	39.15	0·865 . .	·02209	45·26

The numbers in the 4th column are obtained by dividing those of the 3rd column by those of the 2nd; and those in the 5th are obtained by dividing the numbers in the 2nd by those in the 3rd. It will be seen that the numbers in the last two columns are only relative, and that they are inversely proportional to each other. Thus, while the number of atoms of potassium in a given volume is to that of the atoms of carbon in an equal volume as ·02209 to ·5833, or very nearly as 1 to 26·4, the atomic or equivalent volume of potassium is to that of sulphur as 45·26 to 1·714, or very nearly as 26·4 to 1.

This, of course, is on the supposition formerly mentioned, that all atoms have the same specific gravity, and differ in weight from differing in size. But this point, as well as many others connected with the hypothesis of atoms, cannot be determined with certainty; and we must bear in mind that all discussions concerning atomic volumes depend on some such assumption.

Schrœder, and also Kopp, have endeavoured to apply the idea of atomic or equivalent volumes to the purpose of determining by calculation the specific gravity, as well as other physical properties of compounds; and their calculations in many cases have exhibited a wonderful approximation to the results of observation. But in many points their results are very discordant; and the whole subject is surrounded with so many difficulties, that a considerable time must elapse before unlimited confidence can be placed in the results of such calculations.

When we consider that by the term "atom" we must understand not only the indivisible particle of matter, but also the atmosphere of heat, electricity, &c. with which it is surrounded, and when we reflect that these last must be variable, and that chemists are not yet agreed on the question whether matter is porous, or whether, as Le Royer and Dumas, Graham, and Kopp imagine, the space is entirely filled by atoms, without vacant spaces or interstices, it is obvious that much remains to be done before this subject can be profitably discussed in an elementary work.

Playfair and Joule have recently (Phil. Mag., Dec. 1845) endeavoured to show that the volume occupied by compound bodies, such as saline compounds, is always a multiple by a whole number of the volume occupied by an equivalent of water. Their treatise on this subject is very elaborate, and contains many very remarkable facts; but it must be considered still doubtful whether they have established the laws which they announce. They have found it necessary to admit two different values for the equivalent volume of water, and there appears to be no certain rule to point out which of these is to be adopted in any given case. But chemists are much indebted to them for their efforts to throw light on a subject so obscure and so interesting.

CHEMICAL SYMBOLS.

The impracticability in many cases of contriving convenient names expressive of the constitution of chemical compounds, especially of minerals, suggested the employment of symbols as an abbreviated mode of denoting the composition of bodies. It was thought that the names of elementary substances, instead of being written at full length, might often be more conveniently indicated by the first letter of their names; and that the combination of elements with each other might be expressed by placing together, in some way to be agreed on, the letters which represent them. The advantage of such a symbolic language was felt so strongly by Berzelius, that he some years ago contrived a set of symbols, which he has since used extensively in his writings; and other eminent chemists, as well as mineralogists, believing symbols to be useful, adopted those which Berzelius had proposed. The consequence is, that symbolic expressions, called *chemical formulæ*, are now so much resorted to, and are so identified with the language of chemistry, that essays of great value are in a measure as sealed books to those who cannot read symbols. It is therefore important that the chemical student, whatever he may think of the value of symbols, should not be unacquainted with them. Fortunately, the labour of a few minutes will enable him to understand the subject. The following table includes the symbols of all the elementary substances according to Berzelius.

TABLE OF SYMBOLS.

Elements.	Symb.	Elements.	Symb.	Elements.	Symb.
Aluminium	Al	Gold (Aurum)	Au	Potassium (Kalium)	K
Antimony (Stibium)	Sb	Hydrogen	H	Rhodium	R
Arsenic	As	Iodine	I	Ruthenium	Ru
Barium	Ba	Iridium	Ir	Selenium	Se
Bismuth	Bi	Iron (Ferrum)	Fe	Silicon	Si
Boron	B	Lantanium	La	Silver (Argentum)	Ag
Didymium	D	Lead (Plumbum)	Pb	Sodium (Natrium)	Na
Bromine	Br	Lithium	L	Strontium	Sr
Cadmium	Cd	Magnesium	Mg	Sulphur	S
Calcium	Ca	Manganese	Mn	Tellurium	Te
Carbon	C	Mercury (Hydrargyrum)	Hg	Terbium	Tb
Cerium	Ce	Molybdenum	Mo	Thorium	Th
Chlorine	Cl	Niobium	Nb	Tin (Stannum)	Sn
Chromium	Cr	Nickel	Ni	Titanium	Ti
Cobalt	Co	Nitrogen	N	Tungsten (Wolfram)	W
Columbium (Tantalum)	Ta	Osmium	Os	Vanadium	V
Copper (Cuprum)	Cu	Oxygen	O	Uranium	U
Erbium	E	Palladium	Pd	Yttrium	Y
Fluorine	F	Pelopium	Pe	Zinc	Zn
Glucinium	G	Phosphorus	P	Zirconium	Zr
		Platinum	Pl		

For the sake of uniformity, and to prevent confusion, it is much to be wished that these symbols, being now generally known, should be rigorously adhered to. Berzelius has properly selected them from Latin names, as being known to all civilized nations; and when the names of two or more elements begin with the same letter, the distinction is made by means of an additional letter.

The foregoing symbols are intended to represent the chemical eq. of the elements. Thus, the letters H, I, and Ba, stand for 1 eq. of hydrogen, iodine, and barium; and 2 H, 3 H, and 4 H, for 2, 3, and 4 eq. of hydrogen. Two eq. of an element are often denoted by placing a dash through or under its symbol: for instance, ~~H~~ or $\underline{H}$

means 2 H, and $\cancel{\mathrm{P}}$ or $\underline{\mathrm{P}}$ signifies 2 P. Certain compounds are often, for the sake of brevity, denoted by single symbols in the same manner as the elements: thus, an eq. of water, ammonia, and cyanogen is sometimes expressed by Aq, Am, and Cy; but in general the formulæ for compound bodies are so contrived as to indicate the elements they contain, and the mode in which they are united. This may be done in several ways; but that which first suggests itself is, to connect together the symbols by the same signs as are used in Algebra. Thus, the formulæ $\mathrm{K + O}$, $\mathrm{Ca + O}$, $\mathrm{Ba + O}$, $\mathrm{Mn + O}$, $\mathrm{Fe + O}$, $\mathrm{2\ Fe + 3O}$, $\mathrm{3\ H + N}$, $\mathrm{2\ H + 2\ C}$, $\mathrm{C + 2\ O}$, $\mathrm{N + 5\ O}$, $\mathrm{S + 3\ O}$, and $\mathrm{H + Cl}$, denote single eq. of potassa, lime, baryta, protoxide of manganese, protoxide of iron, peroxide of iron, ammonia, olefiant gas, carbonic acid, nitric acid, sulphuric acid, and hydrochloric acid. The formula $\mathrm{K + N + 6\ O}$ indicates the elements which are contained in an eq. of nitrate of potassa: in order to express further that the potassium is combined with only 1 eq. of oxygen, the remaining oxygen with the nitrogen, and the potassa with nitric acid, the symbols are placed thus, $\mathrm{(K + O) + (N + 5\ O)}$, the brackets containing the symbols of those elements which are supposed to be united. A number placed on the outside of a bracket multiplies the compound within it: thus $\mathrm{(K + O) + (S + 3\ O)}$ is sulphate of potassa, and $\mathrm{(K + O) + 2\ (S + 3\ O)}$ is the bisulphate. All the elements contained in a compound are thus visibly represented, and the chemist is able readily to trace all possible modes of combination, and to select that which is most in harmony with the facts and principles of his science. He may, and often does, thereby detect relations which might otherwise have escaped notice.

Another advantage attributable to such formulæ is, that they facilitate the comprehension of chemical changes. If hydrosulphuric acid acts upon the protoxide of lead, it is easy to say that the sulphur combines with the lead, and the hydrogen with the oxygen; but the exact adaptation of the quantities for mutual interchange appears to me more clearly shewn by symbols than by a description or a diagram, both of which are apt to produce confusion where the change to be explained is complex. In the simple instance alluded to, $\mathrm{H + S}$ reacts on $\mathrm{Pb + O}$, and the products are $\mathrm{Pb + S}$ and $\mathrm{H + O}$. When hydrosulphuric acid acts on bicyanuret of mercury, the result is bisulphuret of mercury and hydrocyanic acid: the substances which interchange elements are $\mathrm{2\ (H + S)}$ and $\mathrm{Hg + 2\ Cy}$; and the products are $\mathrm{Hg + 2\ S}$, and $\mathrm{2\ (H + Cy)}$. In more complicated changes the advantage of chemical formulæ is still more manifest, examples of which kind will be found in the section on cyanogen, and in other parts of this volume.

Useful as the algebraic chemical formulæ are for the purpose of studying chemical changes, they are sometimes found inconveniently long where the object is merely to express the composition of bodies, and accordingly Berzelius has introduced several abbreviations. For instance, he indicates degrees of oxidation by dots placed over the symbol, writing $\dot{\mathrm{K}}$, $\ddot{\mathrm{C}}$, $\overset{\cdot\because\cdot}{\mathrm{N}}$, instead of $\mathrm{K} + \mathrm{O}$, $\mathrm{C} + 2\mathrm{O}$, $\mathrm{N} + 5\mathrm{O}$, for potassa, carbonic acid, and nitric acid. In like manner he denotes compounds of sulphur by commas, writing $\overset{,}{\mathrm{K}}$, $\overset{,,}{\mathrm{Hg}}$, $\overset{,}{\mathrm{H}}$, instead of $\mathrm{K} + \mathrm{S}$, $\mathrm{Hg} + 2\,\mathrm{S}$, $\mathrm{H} + \mathrm{S}$, for sulphuret of potassium, bisulphuret of mercury, and hydrosulphuric acid. When the ratio is that of 2 to 3 he employs the symbol for 2 eq. above stated: thus $\overset{\cdots}{\underline{\mathrm{Fe}}}$, $\overset{\cdot\because\cdot}{\underline{\mathrm{P}}}$, $\overset{\cdot\because\cdot}{\underline{\mathrm{As}}}$, is used instead of $2\,\mathrm{Fe} + 3\,\mathrm{O}$, $2\,\mathrm{P} + 5\,\mathrm{O}$, $2\,\mathrm{As} + 5\,\mathrm{O}$, for an equivalent of peroxide of iron, phosphoric acid, and arsenic acid; and similarly we have $\overset{,,,}{\underline{\mathrm{As}}}$, $\overset{,\overset{,\,,}{}\,,}{\underline{\mathrm{As}}}$, instead of $2\ \mathrm{As} + 3\ \mathrm{S}$, $2\ \mathrm{As} + 5\ \mathrm{S}$, for the sesquisulphuret and persulphuret of arsenic. These last formulæ are sometimes used to indicate 2 eq. instead of 1; but as, agreeably to the atomic theory, the smallest possible particle of peroxide of iron consists of 2 atoms of iron and 3 of oxygen, the formula $2\ \mathrm{Fe} + 3\ \mathrm{O}$ ought to stand for 1 eq. only.

Berzelius often dispenses with the sign +, and writes combined elements side by side, the sign of addition being understood instead of expressed. Thus he uses HO, KO, Fe S, $\dot{\mathrm{C}}\mathrm{a}\,\ddot{\mathrm{C}}$, $\dot{\mathrm{B}}\mathrm{a}\,\overset{\cdot\because\cdot}{\mathrm{N}}$, $\dot{\mathrm{K}}\,\dddot{\mathrm{S}} + \dot{\mathrm{N}}\mathrm{i}\,\dddot{\mathrm{S}}$, instead of $\mathrm{H} + \mathrm{O}$, $\mathrm{K} + \mathrm{O}$, $\mathrm{Fe} + \mathrm{S}$, $\dot{\mathrm{C}}\mathrm{a} + \ddot{\mathrm{C}}$, $\dot{\mathrm{B}}\mathrm{a} + \overset{\cdot\because\cdot}{\mathrm{N}}$, $(\dot{\mathrm{K}} + \dddot{\mathrm{S}}) + (\dot{\mathrm{N}}\mathrm{i} + \dddot{\mathrm{S}})$, for water, potassa, sulphuret of iron, carbonate of lime, nitrate of baryta, and the double sulphate of potassa and oxide of nickel. Two or more equivalents of one constituent of a compound are denoted by numbers placed in the same position as the indices of powers in algebra: thus, NH^3, NC^2, $\overset{\cdots}{\underline{\mathrm{Fe}}}{}^2$, $\dot{\mathrm{H}}^3$, is the abbreviation of $\mathrm{N} + 3\,\mathrm{H}$, $\mathrm{N} + 2\,\mathrm{C}$, $2\,\overset{\cdots}{\underline{\mathrm{Fe}}} + 3\,\dot{\mathrm{H}}$, for ammonia, cyanogen, and sesquihydrate of iron, a compound of 2 eq. of peroxide of iron and 3 of water. A number used before symbols, like coefficients in algebra, multiplies all the following symbols not separated from it by a + sign. Thus, in $8\,\dot{\mathrm{C}}\mathrm{a}\,\dddot{\mathrm{S}}\mathrm{i} + \dot{\mathrm{K}}\,\dddot{\mathrm{S}}\mathrm{i}^2 + 16$ aq. (which is the formula for the mineral called apophyllite) the 8 denotes 8 eq. of $\dot{\mathrm{C}}\mathrm{a}\,\dddot{\mathrm{S}}\mathrm{i}$, or silicate of lime, which are united with 1 eq. of bisilicate of potassa, and 16 of water.

Berzelius also expresses the vegetable and animal acids by the first letter of their name, with a dash over it. Thus, $\overline{T}$, $\overline{A}$, $\overline{C}$, $\overline{B}$, $\overline{G}$, $\overline{F}$, are the symbols for tartaric, acetic, citric, benzoic, gallic, and formic acids.

Several objections, some of which are of great weight, have been made to this system of symbols, and various modifications have been proposed by different authors. Among these, that which has been adopted by Liebig and Poggendorff in their Chemical Dictionary, combines more successfully than any other the requisite clearness, brevity, and generality, and will be used in this work. The following are the principles of this method:—The numbers which are written before a symbol affect all that follow as far as the first full stop or sign of addition; while those which are written a little below and to the right hand multiply only the symbol to which they are attached. Two symbols placed side by side are understood to be combined together: thus, HO signifies water; KO potash, &c. When two compounds are separated only by a comma, they are also to be considered as combined. Thus, KO,HO is the symbol of hydrate of potash; KO,SO_3 that of sulphate of potash. When two salts or other complex compounds are combined, the + sign is used: thus, $KO,SO_3 + HO,SO_3$ represents bisulphate of potash, a compound of sulphate of potash with hydrated sulphuric acid. In this system of notation no dots are employed, nor is any abbreviation used to express two equivalents. For example, alumina, which Berzelius abbreviates thus, $\overset{\cdots}{\underline{\mathrm{Al}}}$, is represented by Al_2O_3, which is equally short, more easily written and printed, and which moreover has this advantage, that there is only one symbol used for each element; while the composition of allied compounds admits of a more ready comparison. If, for example, it is wished to show the analogy between the oxides and chlorides of phosphorus, this is at once done by writing their formulæ according to the method of Liebig and Poggendorff:

$$PO_3,\ PO_5;\ PCl_3,\ PCl_5;$$

whereas, if dots are employed for oxygen, the analogy is far from being so obvious:

$$\overset{\cdots}{P},\ \overset{\therefore\cdot\cdot}{P};\ PCl^3,\ PCl^5;$$

unless chlorine be, like oxygen, expressed in two ways; which, however, would embarrass the learner unnecessarily. By comparing the symbol for apophyllite according to Berzelius, above given, with that for the same mineral according to Liebig and Poggendorff, $8\,(CaO, SiO_3) + KO,2SiO_3 + 16\,aq.$, it will be seen that the latter is at least equally clear, and, from the absence of dots, far less liable to error in printing or in reading. In the first limb of the above formula it is to be observed that the figure 8 multiplies all contained within the parenthesis. In like manner, crystallized alum is represented according to Berzelius by $\dot{K}\overset{\cdots}{S} + \overset{\cdots}{\underline{Al}}\,\overset{\cdots}{S}^3 + 24\,\dot{H}$; and, on the method here preferred, by $KO,SO_3 + Al_2O_3,3SO_3 + 24HO$. For the reasons above mentioned, the method of Liebig and Poggendorff will be uniformly employed hereafter; but I have thought it right to explain that of Berzelius, that, where it is met with, it may be understood.

ISOMERIC BODIES.

It was formerly thought that the same elements united in the same ratio must always give rise to the same compound; but within these few years several examples have been discovered of two or even more substances containing the same elements in the same ratio, and yet exhibiting chemical properties distinct from each other. For such compounds Berzelius has suggested the general appellation of *isomeric*, from *ισος equal*, and *μερος part*, expressive of equality in the ingredients. Interesting instances of this kind are the three acids which consist of cyanogen and oxygen in the same ratio, and have the same equivalent, yet differ widely in their chemical properties; and a similar example is afforded by the tartaric and paratartaric acids. Para, from *παρα near to*, is prefixed in order to mark the relation to tartaric acid,—a principle of nomenclature which is extended to some other cases.

Unexpected as was the discovery of isomerism, it is quite consistent with our theories of chemical union, insomuch as the same elements may be grouped or combined in different ways, and thereby give rise to compounds essentially distinct. Thus, the elements of sulphate of potassa may perhaps be united indiscriminately with each other, as expressed by the formula KSO_4; or they may form $KO + SO_3$; or $KS + O_4$; or $KO_2 + SO_2$; and other combinations might be made. The second of these is thought to be the real one; but no one can say that the others are impracticable. Again, the elements of peroxide of tin, Sn and 2O, may either form SnO_2, or $SnO + O$; and those of the peroxide of iron, 2Fe and 3O, may either be Fe_2O_3, or $FeO + FeO_2$, not to mention other possible combinations. The elements of alcohol are 4C, 6H, and 2O, which may be united indiscriminately as $C_4H_6O_2$, $C_4H_6 + 2O$, $C_4H_5O + HO$, or $C_4H_4 + 2HO$, besides others.

Bodies may be said, in a general sense, to be *isomeric*, when the relative proportions of their ingredients are the same, without reference to the absolute number of atoms of each element, or the equivalents of the compound. But we must distinguish two cases of isomerism.

In the first, not only are the relative proportions of the elements the same, but also the absolute number of atoms of each element, and consequently the equivalent or atomic weights of the compounds. Thus, acetate of oxide of ethyle and hydrated butyric acid have both a composition represented by the empirical formula $C_8H_8O_4$; hyduret of salicyle and hydrated benzoic acid have both the empirical formula $C_{14}H_6O_4$, Such compounds are properly *isomeric.*

The second case of isomerism is that of bodies in which, while the relative proportions of the elements are the same, the absolute number of atoms of each element, and consequently the equivalent or atomic weights of the compounds, differ. Thus, aldehyde has the same composition in 100 parts, that is, the same relative proportion of the elements, as acetate of oxide of ethyle and hydrated butyric acid. But while the empirical formula of the two latter is $C_8H_8O_4$, that of the former is $C_4H_4O_2$, or exactly one half. Again, cyanic acid, fulminic acid, and cyanuric acid have exactly the same composition in 100 parts; but their empirical formulæ are respectively C_2NHO_2, $C_4N_2H_2O_4$, and $C_6N_3H_3O_6$, the absolute number of atoms, and consequently the atomic weights of the three compounds, being as 1, 2, and 3. Such compounds, are called *polymeric.* This case is of very frequent occurrence.

There is another distinction to be made in regard to bodies properly isomeric. When the absolute number of atoms, and consequently the atomic weight of two or more compounds, is the same, we can hardly suppose the grouping or arrangement to be also the same. Indeed, were we to assume this, we could not see how the properties of the compounds could be different, since the same number of atoms similarly grouped must necessarily possess the same properties. It appears, therefore, evident, that, where two compounds are isomeric, the atoms must be differently grouped, if the equivalents are equal.

In most known cases of isomerism we admit this difference of grouping or arrangement. Thus, to take the case of acetate of oxide of ethyle and butyric acid, while the *empirical* formula of both is $C_8H_8O_4$, the *rational* formula of the former is $C_4H_5O + C_4H_3O_3$; and that of the latter is $C_8H_7O_3 + HO$. In like manner, the empirical formula of hydrated benzoic acid and of hyduret of salicyle is $C_{14}H_6O_4$; the rational formula of the former is $C_{14}H_5O_3 + HO$, and that of the latter $C_{14}H_5O_4 + H$. The rational formula is that which expresses the view we take of the *constitution* of a compound: that is, of the grouping or arrangement of the atoms. Taking this circumstance into consideration, compounds thus related are strictly called *metameric;* so that we cannot say that any compounds absolutely isomeric exist, although the term is commonly applied to the bodies here called metameric.

In the case of polymeric bodies, a difference in the grouping of the atoms is not absolutely necessary, since, if a different number of atoms be grouped alike, we can still conceive the result to be different. But even in this case we have reason to believe that there is generally a difference in the grouping of the atoms. Thus, aldehyde and acetate of oxide of ethyle are polymeric, as above stated, but the rational formula of the former is $C_4H_3O + HO$, while that of the latter is $C_4H_5O + C_4H_3O_3$.

The idea has been started by some chemists, that, as in polymeric compounds a difference in the absolute number of atoms causes a difference in properties, whether the grouping be the same or not, so it is possible that the atoms of a simple substance, if aggregated into molecules containing different numbers of atoms, may give rise to new properties even in elementary substances, in other words, to what has been called isomeric (more properly polymeric) transmutation of elements. But the cases are obviously quite distinct.

It would be going too far to declare that this transmutation is impossible; but it is evident that it is not consistent with our present views of the nature of elements. If each atom of an element possess the properties of that element, it is contradictory to suppose that mere aggregation can confer new chemical properties; since we are only acquainted with aggregates of atoms, and these aggregates, ex hypothesi, possess the same properties as the atoms of which they are made up. It may be said, indeed, that our hypothesis is not demonstrable, and that, for aught we know, the atoms may not have the properties of the aggregates which they form; but this is at least as little capable of demonstration as the ordinary view; and, in favour of the latter, we know that very great changes in aggregation do occur without affecting the chemical properties of elementary bodies. Thus, sulphur, for example, is still sulphur, whether it be solid, liquid, or gaseous.

Admitting the existence of atoms, it would appear that they cannot have all the physical properties of the aggregate masses of matter which they make up: for this reason, that many of those properties depend on the aggregation of atoms. Thus, transparency, opacity, colour, hardness, porosity, compressibility, and the like, are properties of aggregates or compound molecules, and not of atoms. But it is difficult to conceive the existence of atoms at all, unless we admit that the atoms of different elements do really differ in chemical properties, or, at least, in the power of exhibiting such properties when aggregated into compound molecules.

Some attempts have indeed been made to demonstrate experimentally the possibility of the isomeric (polymeric) transmutation of elements; and if this could be done there would be an end of the question, and we should have to modify our ideas of atoms and of elements.

Dr. Samuel Brown has published, in the Transactions of the Royal Society of Edinburgh, some experiments from which he drew the conclusion that carbon, under certain circumstances, might be transmuted into silicon, and he also stated that he had succeeded in transmuting iron into rhodium. His idea would appear to be that the atoms of carbon, by being aggregated in a different manner from that which prevails in carbon, produce a body having the properties of silicon, but still elementary, as containing only one kind of matter. It is impossible here to enter into a detail of his experiments: it is sufficient to say that no one has yet succeeded in obtaining the same results, and that Dr. Wilson, Dr. Tilley, and others have rendered it highly probable that Dr. Brown has been misled by the presence of impurities in the materials on which he operated. Dr. Wilson, indeed, inclines to the doctrine of isomeric transmutation of elements, but hitherto no evidence has been produced, of an experimental nature, such as to render that doctrine even probable.

In conclusion, it may be observed, that, as there is reason to admit some kind of grouping of the atoms of elementary bodies as necessary to their existence with the properties which we consider to belong to the elements, so a different grouping, with different properties as its results, may be considered possible, although, if the prevalent ideas respecting atoms be correct, it is very far from being probable, and certainly has hitherto received no support from experiment. Moreover, we shall see hereafter, that in sulphur and some other elements modifications called *allotropic* actually exist, in which we can only suppose the difference of properties to arise from a difference in the aggregation of the atoms to form molecules. But in all known cases of allotropic modification, and these are now pretty numerous, the modified forms retain the essential properties of the element, and do not exhibit any appearance of transmutation. The principle, however, of difference of properties, as a consequence of a difference either in the number or the grouping of the same elements, combined in the same proportion, when applied to *compound bodies*, is one of the highest importance, and plays a most essential part in the chemistry of organized bodies.

SECTION III.

OXYGEN.

History.—Discovered by Priestley in 1774, and by Scheele a year or two after, without previous knowledge of Priestley's discovery. It was termed *Dephlogisticated air* by Priestley, *Empyreal air* by Scheele, and *Vital air* by Condorcet. The name it now bears, derived from the Greek words οξυς *acid* and γενναειν *to generate*, was proposed by Lavoisier, who considered it the sole cause of acidity.

Preparation.—From several sources; the peroxides of manganese, lead, and mercury, nitre, and chlorate of potassa, yield it in large quantities when they are exposed to a red heat. The substances commonly employed for the purpose are peroxide of manganese and chlorate of potassa. It may be procured from the former in two ways: either by heating it to redness in a gun-barrel, or in a retort of iron or earthenware; or by putting it in fine powder into a flask with about an equal weight of concentrated sulphuric acid, and heating the mixture by means of a lamp. To understand the theory of these processes, it is necessary to bear in mind the composition of the three following oxides of manganese:—

	Manganese.	Oxygen.	
Protoxide	27·7 or 1 equiv.	+ 8	= 35·7
Sesquioxide	27·7	+ 12	= 39·7
Peroxide	27·7	+ 16	= 43·7

On applying a red heat to the last, it parts with half an equivalent of oxygen, and is converted into the sesquioxide. Every 43·7 grains of the peroxide will therefore lose, if quite pure, 4 grains of oxygen, or nearly 12 cubic inches; and one ounce will yield about 128 cubic inches of gas. With sulphuric acid the peroxide loses a whole eq. of oxygen, and is converted into the protoxide, which unites with the acid, forming a sulphate of the protoxide of manganese. Every 43·7 grains of peroxide yields 8 grains of oxygen and 35·7 of protoxide, which, by uniting with one eq. (40) of the acid, forms 75·7 of the sulphate. The first of these processes is the most convenient in practice.

The gas obtained from peroxide of manganese, though hardly ever quite pure, owing to the presence of carbonate of lime and other earthy substances, besides traces of organic matter, is sufficiently good for ordinary purposes. It yields a gas of better quality, if previously freed from carbonate of lime by dilute hydrochloric or nitric acid; but when oxygen of great purity is required, it is better to obtain it from chlorate of potassa. For this purpose, the salt should be put into a retort of green glass, or of white glass made without lead, and be heated nearly to redness. It first becomes liquid, though quite free from water, and then, on increase of heat, is wholly resolved into pure oxygen gas, which escapes with effervescence, and into a white compound, called chloride of potassium, which is left in the retort. The composition of the chloric acid and potassa, which constitute the salt, is stated below:—

Chlorine .	35·42 or 1 eq.	Potassium .	39·15 or 1 eq.
Oxygen .	40·00 or 5 eq.	Oxygen .	8·00 or 1 eq.
Chloric Acid .	75·42 or 1 eq.	Potassa .	47·15 or 1 eq.

Hence the oxygen which passes over from the retort is derived partly from the potassa and partly from the chloric acid; while chlorine and potassium enter into combination. Thus are 122·57 grains of the chlorate resolved into 74·57 grains of chloride of potassium, and 48 grains, or about 161 cubic inches of pure oxygen. The following equation briefly and clearly explains the change, $KO + ClO_5 = KCl + O_6$.

The process just described is very much facilitated by mixing with the chlorate from $\frac{1}{10}$ to $\frac{1}{4}$ of its weight of peroxide of manganese. The gas now comes off very rapidly on the application of a gentle heat; and so violent is the action, that a glow of red heat passes through the mass in the retort, while externally it is far below a red heat. The gas is given off so rapidly, that, unless a very wide exit be afforded to it, it is apt to burst the vessel, or force out the tube, if a flask be used with a tube fitted into the cork. It is not known with certainty how the oxide of manganese acts in promoting the decomposition of the chlorate. The oxide is found unchanged after the operation, or it may even have lost part of its own oxygen by the heat generated. Other substances may be substituted for the oxide of manganese, such as oxide of copper, and, according to some, powdered pumice-stone, or any similar substance. The action is probably mechanical, the points of the powder affording so many centres of gasification, as when the boiling of water is facilitated by the introduction of iron filings.

Another method of obtaining oxygen gas has lately been introduced, which may often prove convenient. It is to mix bichromate of potassa with sulphuric acid into a thin paste, and apply a moderate heat to the mixture, in a florence flask furnished with a tube. Here the bichromate $KO,2CrO_3$ loses 3 eq. of oxygen, and there are left the potassa, KO, and sesquioxide of chromium, Cr_2O_3, both combined with sulphuric acid. The following equation exhibits the change, $(KO,2CrO_3) + 4(SO_3,HO) = (KO,SO_3) + (Cr_2O_3,3SO_3) + 4HO + O_3$.

Properties.—Colourless, tasteless, inodorous; it refracts light feebly, and is a non-conductor of electricity; heavier than atmospheric air, its sp. gr. being estimated at 1·1026 by Dulong and Berzelius, so that 100 cubic inches weigh at 60° and 30′ Bar. 34·193 grains. It is always gaseous when not combined with other ponderable matter; though even in its simplest form it is associated, like other elementary principles, with the agents productive of heat, light, and electricity. Like all gases it emits a strong heat when suddenly compressed: light also appears; but this is solely due to its chemical action on the oil with which the compressing tube is lubricated. It is the most perfect − electric, always appearing at the + electrode when any of its compounds is electrolized; is sparingly absorbed by water, which dissolves only 3 or 4 per cent. of the gas; is neither acid nor alkaline, as it does not change the colour of blue flowers, nor evince a disposition to unite directly either with acids or alkalies. It has a very powerful attraction for most simple substances; and there is not one of them, except perhaps the highly-negative fluorine, with which it may not be made to combine. The act of combining with oxygen is called *oxidation*, and bodies which have united with it are said to be *oxidized.* The compounds so formed are divided by chemists into acids and oxides. The former division includes those compounds which possess the general properties of acids; and the latter comprehends those which not only do not possess that character, but of which many are highly alkaline, and yield salts by uniting with acids. The phenomena of oxidation are variable. It is sometimes produced with great rapidity, and with evolution of heat and light. Ordinary combustion, for instance, is nothing more than rapid oxidation; and all inflammable or combustible substances derive their power of burning in the open air from their affinity for oxygen. On other occasions it takes place slowly, and without any appearance either of heat or light, as in the rusting of iron by moist air. Different as these processes may appear, oxidation is the result of both; and both depend on the same circumstance, namely, the presence of oxygen in the atmosphere. Another example of gradual oxidation is the decay or eremacausis (slow combustion) of organic matter, whether animal or vegetable, when exposed to the air. By virtue of this process, all dead organized bodies are finally resolved into those forms of combination in which they serve as food for new generations of plants, which in their turn afford nourishment to new generations of animals.

All substances that are capable of burning in the open air, burn with far greater brilliancy in oxygen gas. A piece of wood, on which the least spark of light is visible, bursts into flame the moment it is put into a jar of oxygen; lighted charcoal emits beautiful scintillations; and phosphorus burns with so powerful and dazzling a light, that the eye cannot bear its impression. Even iron and steel, which are not commonly ranked among the inflammables, undergo rapid combustion in oxygen gas.

The changes that accompany these phenomena are no less remarkable than the phenomena themselves. When a lighted taper is put into a vessel of oxygen gas, it burns for a while with increased splendour; but the size of the flame soon begins to diminish, and if the mouth of the jar be closed, the light will in a short time disappear entirely. The gas has now lost its characteristic property; for a second lighted taper, immersed in it, is instantly extinguished. This result is general. The burning of one body in a given portion of oxygen unfits it more or less completely for supporting the combustion of another; and the reason is manifest. Combustion is produced by the combination of inflammable matter with oxygen. The quantity of free oxygen, therefore, diminishes during the process, and is at length nearly or quite exhausted. The burning of all bodies, however inflammable, must then cease, because the presence of oxygen is necessary to its continuance. For this reason oxygen gas is called a supporter of combustion. Oxygen often loses its gaseous form as well as its other properties. If phosphorus or iron be burned in a jar of pure oxygen over water or mercury, the disappearance of the gas becomes obvious by the ascent of the liquid, which is forced up by the pressure of the atmosphere, and fills the vessel. Sometimes, on the contrary, the oxygen gas suffers diminution of volume only, or it may even undergo no change of bulk at all, as is exemplified by the combustion of the diamond.

The changes experienced by the burning body are equally striking. While the oxygen loses its power of supporting combustion, the inflammable substance lays aside its combustibility. It is then an oxidized body, and cannot be made to burn even by aid of the purest oxygen gas. It has also increased in weight. It is an error to suppose that bodies lose anything while they burn. The materials of our fires and candles do indeed disappear, but they are not destroyed. Although they fly off in the gaseous form, and are commonly lost to us, it is not difficult to collect and preserve all the products of combustion. When this is done with the required care, the combustible matter is always found to weigh more after than before combustion; and the increase in weight is exactly equal to the quantity of oxygen which has disappeared during the process.

Oxygen gas is necessary to respiration. No animal can live in an atmosphere which does not contain a certain portion of uncombined oxygen; for an animal soon dies if placed in a portion of air from which the oxygen has been previously removed by a burning body. Oxygen disappears during respiration. If a bird be confined in a limited quantity of atmospheric air, it will at first feel no inconvenience; but as a portion of oxygen is withdrawn at each inspiration, its quantity diminishes rapidly, so that respiration soon becomes laborious, and in a short time ceases altogether. Should another bird be then introduced into the same air, it will die in the course of a few seconds; or if a lighted candle be immersed in it, its flame will be extinguished. Respiration and combustion have therefore the same effect. An animal cannot live in an atmosphere which is unable to support combustion; nor, in general, can a candle burn in air which contains too little oxygen for respiration.

It is singular, that, though oxygen is necessary to respiration, in a state of purity it is deleterious. When an animal, as a rabbit for example, breathes pure oxygen gas, no inconvenience is at first perceived; but after the interval of an hour or more the circulation and respiration become very rapid, and the system in general is highly excited. Symptoms of debility subsequently ensue, followed by insensibility; and death occurs in six, ten, or twelve hours. On examination after death, the blood is found highly florid in every part of the body, and the heart acts strongly even after the breathing has ceased. For these experiments we are indebted to Broughton. The eq. of oxygen is = 8; eq. vol. = 50; symb. O.

THEORY OF COMBUSTION.

The only phenomena of combustion noticed by an ordinary observer are, the destruction of the burning body, and the developement of heat and light; but it has been demonstrated that in addition to these circumstances, oxygen gas invariably disappears, and a new compound consisting of oxygen and the combustible is generated. The term *combustion*, therefore, in its common signification, implies the rapid union of oxygen gas and combustible matter, accompanied with heat and light. As the evolution of heat and light is dependent on chemical action, the same phenomena may be expected in other chemical processes; and accordingly heat and light are frequently emitted quite independently of oxygen. Thus phosphorus takes fire, and a taper burns for a short time, in a vessel of chlorine; and several of the common metals, such as copper, antimony, and arsenic, in a state of fine division, become red hot when introduced into a jar of that gas. Potassium takes fire in cyanogen gas; and copper leaf or iron wire, if moderately heated, undergoes the same change in the vapour of sulphur. A mixture of iron filings and sulphur, when heated so as to bring the latter into perfect fusion, emits intense heat and light at the instant of combination; and a like effect, though in a far less degree, is produced by the action of concentrated sulphuric acid on pure magnesia. Most of these and similar examples, especially when one of the combining substances is gaseous, are frequently included under the idea of combustion; and they certainly belong to the same class of phenomena.

In all cases of combustion, in which one of the combining bodies is gaseous, the heat and light appear to proceed from the solid or liquid body; but this is because the combination can only occur where the two bodies are in contact. The heat and light do not really proceed from one body more than from the other, but are simply the result of combination. By a little contrivance, they may be made to appear to come from the oxygen, and not from what is usually called the combustible. Thus, if a jet of hydrogen gas be set fire to in a vessel of oxygen or of chlorine, the heat and light appear to proceed from the jet of hydrogen; but if a jet of oxygen or chlorine gas be set fire to in a vessel of hydrogen, they burn, and the heat and light appear to come from the jet of oxygen. In this last experiment we might call oxygen and chlorine combustibles, and hydrogen a supporter of combustion. But the truth is that both are equally combustibles and supporters of combustion, the heat and light in both experiments being derived from the combination of the two bodies. In the subsequent observations, however, I shall employ the term combustion in its ordinary sense; but the remarks concerning increase of temperature, whether with or without light, apply equally to all cases where heat is developed as a result of chemical action.

For many years prior to the discovery of oxygen gas, the phenomena of combustion were explained on the Stahlian or phlogistic hypothesis. All combustible bodies, according to Stahl, contain a certain principle which he called *phlogiston*, to the presence of which he ascribed their combustibility. He supposed that when a body burns, phlogiston escapes from it; and that when the body has lost phlogiston, it ceases to be combustible, and is then a dephlogisticated or incombustible substance. A metallic oxide was consequently regarded as a simple substance, and the metal itself as a compound of its oxide with phlogiston. The heat and light which accompany combustion were attributed to the rapidity with which phlogiston is evolved during the process.

The discovery of oxygen proved fatal to the Stahlian doctrine. Lavoisier had the honour of overthrowing it, and of substituting in its place the antiphlogistic theory. The basis of his doctrine has already been stated,—that combustion and oxidation in general consist in the combination of combustible matter with oxygen. This fact he established beyond a doubt. On burning phosphorus in a jar of oxygen, he observed that a considerable quantity of the gas disappeared, that the phosphorus gained materially in weight, and that the increase of the latter exactly corresponded to the loss of the former. An iron wire was burnt in a similar manner, and the weight of the oxidized iron was found equal to that of the wire originally employed, added to the quantity of oxygen which had disappeared. That the oxygen is really present in the oxidized body, he proved by a very decisive experiment. Some liquid mercury was confined in a vessel of oxygen gas, and exposed to a temperature sufficient for causing its oxidation. The oxide of mercury, so produced, was put into a small retort and heated to redness, when it was reconverted into oxygen and fluid mercury, the quantity of the oxygen being exactly equal to that which had combined with the mercury in the first part of the operation.

To account for the production of heat and light during combustion, Lavoisier had recourse to Black's theory of latent heat. Heat is always evolved when a substance, without change of form, passes from a rarer into a denser state, and also when a gas becomes liquid or solid, or a liquid solidifies ; because a quantity of heat previously combined, or latent, within it, is then set free. Now this is precisely what happens in many instances of combustion. Thus water is formed by the burning of hydrogen, in which case two gases give rise to a liquid ; and in forming phosphoric acid with phosphorus, or in oxidizing metals, oxygen is condensed into a solid. When the product of combustion is gaseous, as in the burning of charcoal, the evolution of heat is ascribed to the circumstance that the oxidized body contains a smaller quantity of combined heat, or has a smaller sp. heat, than the substances by which it is produced.

This is the weak point of Lavoisier's theory. Chemical action is very often accompanied by increase of temperature, and the heat evolved during combustion is only a particular instance of it. Any theory, therefore, by which it is proposed to account for the production of heat in some cases, ought to be applicable to all. When combustion, or any other chemical action, is followed by considerable condensation, in consequence of which the new body contains less insensible heat than its elements did before combination, it is obvious that heat will, in that case, be disengaged. But if this were the sole cause of the phenomenon, a rise of temperature should always be preceded by a corresponding diminution of sp. heat, and the extent of the former ought to be in a constant ratio with the degree of the latter. Now Petit and Dulong infer from their researches on this subject (An. de Ch. et Ph. x.), that the degree of heat developed during combination bears no relation to the sp. heat of the combining substances; and that, in the majority of cases, the evolution of heat is not attended by any diminution in the sp. heat of the compound. It is a well-known fact, that increase of temperature frequently attends chemical action, though the products contain much more insensible heat than the substances from which they were formed. This happens remarkably in the explosion of gunpowder, which is attended by intense heat; and yet its materials, in passing from the solid to the gaseous state, expand to at least 250 times their volume, and consequently render latent a large quantity of heat.

These circumstances leave no doubt that the evolution of heat during chemical action is owing to some cause quite unconnected with that assigned by Lavoisier; and if this cause operates so powerfully in some cases, it is fair to infer that part of the effect must be owing to it on those occasions when the phenomena appear to depend on change of sp. heat alone. A new theory is therefore required to account for the chemical production of heat. But it is easier to perceive the fallacies of one doctrine, than to substitute another which shall be faultless; and it appears to me that chemists must, for the present, be satisfied with the simple statement, that energetic chemical action does of itself give rise to increase of temperature. Berzelius, in adopting the electro-chemical theory, regards the heat of combination as an electrical phenomenon, believing it to arise from the oppositely electrical substances neutralizing one another, in the same manner as the electric equilibrium is restored during the discharge of a Leyden jar. Electrical action certainly appears to be an essential part of every chemical change, and it is probable that the heat developed during the latter may be due to the former; but this part of science is as yet too imperfect for indicating the precise mode by which the effect is produced.

The heat emitted during combustion varies with the nature of the material. The effect of the combustible gases in raising the temperature of water, according to the experiments of Dalton, is shewn in the following table.—(Chemical Philosophy, ii. 309.)

Hydrogen, in burning, raises an equal volume of water	5° F.
Carbonic Oxide	4½
Light Carburetted Hydrogen	18
Olefiant Gas	27
Coal Gas, varies with the quality of the gas from	10 to 16
Oil Gas, varies also with the quality of the gas from	12 to 20

Dalton further states that generally the combustible gases give out heat nearly in proportion to the oxygen which they consume.

Despretz has given a notice of some experiments on the heat developed in combustion (An. de Ch. et Ph. xxxvii. 180). The substances burned were hydrogen, carbon, phosphorus, and several metals; and so much of each was employed as to require the same quantity of oxygen. When the combustion of hydrogen gas produced 2578 degrees of heat, carbon gave out 2967, and iron 5325. Phosphorus, zinc, and tin emit quantities of heat very nearly the same as iron. Hence it follows that, for equal quantities of oxygen, hydrogen in burning evolves less heat than most other substances. These results do not accord with those of Dalton.

SECTION IV.

HYDROGEN.

Hist.—First correctly described in 1766 by Cavendish (Phil. Trans. lvi. 144), under the name of *inflammable air.* It had been previously confounded with other combustible gases, and it was by some called *phlogiston,* from the notion that it is the matter of heat. Its present name is derived from *ὑδωρ water,* and *γενναειν to generate.*

Prep.—Commonly in two ways. The first consists in passing the vapour of water over metallic iron heated to redness. This is done by putting iron wire into a gun-barrel open at both ends, to one of which is attached a retort containing pure water, and to the other a bent tube. The gun-barrel is placed in a furnace, and when it has acquired a full red heat, the water in the retort is made to boil briskly. The gas, which is copiously disengaged as soon as the steam comes in contact with the glowing iron, passes along the bent tube, and may be collected in convenient vessels, by dipping the free extremity of the tube into the water of a pneumatic trough. The second and more convenient method consists in putting pieces of iron or zinc into dilute sulphuric acid, formed of one part of strong acid and four or five of water. Zinc is generally preferred. The hydrogen obtained in these processes is not absolutely pure. The gas evolved during the solution of iron has an offensive odour, ascribed by Berzelius to the presence of a volatile oil, which may be almost entirely removed by transmitting the gas through alcohol. The oil appears to arise from some compound being formed between hydrogen and the carbon which is always contained even in the purest kinds of common iron; and it is probable that a little carburetted hydrogen gas is generated at the same time. The zinc of commerce contains sulphur, and almost always traces of charcoal, in consequence of which it is contaminated with hydro-sulphuric acid, and probably with the same impurities, though in a less degree, as are derived from iron. A little metallic zinc is also contained in it, apparently in combination with hydrogen. All these impurities, carburetted hydrogen excepted, may be removed by passing the hydrogen through a solution of pure potassa. To obtain hydrogen of great purity distilled zinc should be employed.

Prop.—Colourless, inodorous, tasteless; always gaseous when uncombined; a powerful refractor of light; the lightest body in nature, and hence the best material for filling balloons. From its extreme lightness it is difficult to ascertain its sp. gr. by weighing, because the presence of minute quantities of common air or watery vapour occasions considerable error. By the table of sp. gravities (page 163) it appears that hydrogen gas is just 16 times lighter than oxygen, an inference derived from the composition of water to be shortly stated: hence 100 C. I. 60° and 30′ Bar. should weigh $\frac{1}{16} \times 34{\cdot}193 = 2{\cdot}1371$ grains, and its sp. gr. should be 0·06896. Hydrogen gas has not yet been reduced to the liquid state, although it has been exposed to a very high pressur, combined with intense cold.

It is neither acid nor alkaline. Water dissolves only 1½ per cent. of its volume. It cannot support respiration: death ensues from deprivation of oxygen rather than from any noxious quality of the hydrogen, since an atmosphere composed of a due proportion of oxygen and hydrogen gases may be respired without inconvenience. Nor is it a supporter of combustion; for when a lighted candle, fixed on wire, is passed up into an inverted jar full of hydrogen gas, the light instantly disappears.

Hydrogen gas is inflammable in an eminent degree, though, like other combustibles, it requires the aid of a supporter of combustion, burning only where it is in contact with the air. Its combustion, when conducted in this manner, goes on tranquilly, and is attended with a pale yellowish flame and a very feeble light. The phenomena are different when the hydrogen is previously mixed with a due quantity of air. The approach of flame not only sets fire to the gas near it, but the whole is kindled at the same instant; and a flash of light passes through the mixture, accompanied by a violent explosion. The best proportion for the experiment is two measures of hydrogen to five or six of air. The explosion is far more violent when pure oxygen is used instead of atmospheric air, particularly when the gases are mixed together in the ratio of one measure of oxygen to two of hydrogen.

Oxygen and hydrogen gases cannot combine at ordinary temperatures, and may, therefore, be kept in a state of mixture without even gradual combination taking place between them. Hydrogen may be set on fire, when in contact with air or oxygen gas, by flame, by a solid body heated to bright redness, and by the electric spark. If a jet of hydrogen gas be thrown upon recently prepared spongy platinum, this metal almost instantly becomes red hot, and then sets fire to the gas, a discovery which was made in the year 1824 by Professor Doebereiner of Jena. The power of flame and electricity in causing a mixture of hydrogen with air or oxygen gas to explode, is limited. Mr. Cavendish found that flame occasions a very feeble explosion when the hydrogen is mixed with nine times its bulk of air; and that a mixture of four measures of hydrogen with one of air does not explode at all. An explosive mixture formed of two measures of hydrogen and one of oxygen gas, explodes from all the causes above enumerated. Biot found that sudden and violent compression likewise causes an explosion, apparently from the heat emitted during the operation; for an equal degree of condensation, slowly produced, has not the same effect. The electric spark ceases to cause detonation when the explosive mixture is diluted with twelve times its volume of air, fourteen of oxygen, or nine of hydrogen; or when it is expanded to sixteen times its bulk by diminished pressure. Spongy platinum acts just as rapidly as flame or the electric spark in producing explosion, provided the gases are quite pure and mixed in the exact ratio of two to one.* Mr. Faraday finds that platinum foil, if perfectly clean, produces gradual though rather rapid combination of the gases, often terminating in explosion, from the temperature rising to a red heat before all the mixture has disappeared. (Phil. Trans. 1834.)

When the action of heat, the electric spark, and spongy platinum no longer cause explosion, a silent and gradual combination between the gases may still be occasioned by them. Sir H. Davy observed that oxygen and hydrogen gases unite slowly with one another, when they are exposed to a temperature above the boiling point of mercury, and below that at which glass begins to appear luminous in the dark. An explosive mixture diluted with air to too great a degree to explode by electricity, is made to unite silently by a succession of electric sparks. Spongy platinum causes them to unite slowly, though mixed with one hundred times their bulk of oxygen gas.

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* For a variety of facts respecting the causes which prevent the action of flame, electricity, and platinum in producing detonation, the reader may consult the Essay of M. Grotthus in the Ann. de Chimie, vol. lxxxii.; Sir H. Davy's work on Flame; Dr. Henry's Essay in the Philosophical Transactions for 1824; and a paper by myself in the Edinburgh Philosophical Journal for the same year.

A large quantity of heat is evolved during the combustion of hydrogen gas. Lavoisier concludes from experiments made with his calorimeter (Elements, vol. i.), that one pound of hydrogen occasions as much heat in burning as is sufficient to melt 295·6 pounds of ice. Dr. Dalton fixes the quantity of ice at 320 pounds, and Dr. Crawford at 480. The most intense heat that can be produced, is caused by the combustion of hydrogen in oxygen gas. Dr. Hare of Philadelphia, who first burned hydrogen for this purpose, collected the gases in separate gas-holders, from which a stream was made to issue through tubes communicating with each other, just before their termination. At this point the jet of the mixed gases was inflamed. The effect of the combustion, though very great, is materially increased by forcing the two gases in due proportion into a strong metallic vessel by means of a condensing syringe, and setting fire to a jet of the mixture as it issues. An apparatus of this kind, now known by the name of the oxy-hydrogen blowpipe, was contrived by Mr. Newman, and employed by the late Professor Clarke in his experiments on the fusion of refractory substances. On opening a stop-cock which confines the compressed gases, a jet of the explosive mixture issues with force through a small blowpipe tube, at the extremity of which it is kindled. In this state, however, the apparatus should never be used; for as the reservoir is itself full of an explosive mixture, there is great danger of the flame running back along the tube, and setting fire to the whole gas at once. To prevent the occurrence of such an accident, which has sometimes proved fatal to the operator, Professor Cumming proposed that the gas, as it issues from the reservoir, should be made to pass through a cylinder full of oil or water before reaching the point at which it is to burn; and Dr. Wollaston suggested the additional precaution of fixing successive layers of fine wire gauze within the exit tube, each of which would be capable of intercepting the communication of flame. A modification of this apparatus has been devised by Mr. Gurney; but both his and Newman's are rendered unnecessary by the safety tube lately proposed by Mr. Hemming. It consists of a brass cylinder, about 6 inches long, and 3-4ths of an inch wide, filled with very fine brass wire in length equal to that of the tube. A pointed rod of metal, 1-8th of an inch thick, is then forcibly inserted through the centre of the bundle of wires in the tube, so as to wedge them tightly together. The interstices between the wires thus constitute very fine metallic tubes, the conducting power of which is so great as entirely to intercept the passage of flame. The mixed gases are supplied from a common bladder. (Phil. Mag., 3rd S., i. 82.) A very intense heat may be safely and easily procured by passing a jet of oxygen gas through the flame of a spirit lamp, as proposed by the late Dr. Marcet. An elegant improvement on this principle has been devised by Mr. Daniell, by fixing a jet for conveying oxygen within another jet for hydrogen or coal gas, so that a current of oxygen may be introduced into the middle of the flame. (Phil. Mag. ii. 57, 3rd Series.) The heat from this apparatus is quite sufficient for most purposes; and it may be still further increased by causing the gases to pass separately through heated tubes, in order that they may have a temperature of 400° or 500° on issuing from the jets. — On this principle, first employed by Mr. Neilson of Glasgow, is founded the patent of Mr. Dunlop, of the Carron Iron Works, for increasing the temperature of blast furnaces: the air which supports the combustion is previously heated by transmission through iron tubes kept at a low red heat, whereby the power of the furnaces is surprisingly increased, and a great saving in fuel and time is accomplished.

Its eq. is = 1; eq. vol. = 100; symb. H. Compounds with oxygen:—

	By Weight.			By Volume.	
	Hydrogen.	Oxygen.	Equiv.	Hyd.	Oxy.
Water (Protoxide of Hydrogen)	1 or 1 eq. +	8 or 1 eq. =	9	100	50
Peroxide of Hydrogen	[illegible] or 1 eq. +	16 or 2 eq. =	17	100	100

Water.—First proved by Cavendish to be the sole product of the combustion of hydrogen gas. He demonstrated it by burning oxygen and hydrogen gases in a dry glass vessel, when a quantity of pure water was generated, exactly equal in weight to that of the gases which had disappeared. This experiment, which is the synthetic proof of the composition of water, was afterwards made on a much larger scale in Paris by Vauquelin, Fourcroy, and Seguin. Lavoisier first demonstrated its nature analytically, by passing a known quantity of watery vapour over metallic iron heated to redness in a glass tube. Hydrogen gas was disengaged, the metal in the tube was oxidized, and the weight of the former, added to the increase which the iron had experienced from combining with oxygen, exactly corresponded to the quantity of water decomposed.

Its composition by volume was demonstrated very satisfactorily by Nicholson and Carlisle: by resolving water into its elements by galvanism, and collecting them in separate vessels, they obtained precisely two measures of hydrogen and one of oxygen, — a result which has been fully confirmed by subsequent experimenters. The same fact was proved synthetically by Gay-Lussac and Humboldt, in their Essay on Eudiometry, published in the *Journal de Physique* for 1805. They found that when a mixture of oxygen and hydrogen is inflamed by the electric spark, those gases always unite in the exact ratio of one to two, whatever may be their relative quantity in the mixture. When one measure of oxygen is mixed with three of hydrogen, one measure of hydrogen remains after the explosion ; and a mixture of two measures of oxygen and two of hydrogen leaves one measure of oxygen. When one volume of oxygen is mixed with two of hydrogen, both gases, if quite pure, disappear entirely on the electric spark being passed through them. The composition of water by weight was determined with great care by Berzelius and Dulong; and we cannot hesitate, considering the known dexterity of the operators, and the principle on which their method of analysis was founded, to regard their result as a nearer approximation to the truth than that of any of their predecessors. They state, as a mean of three careful experiments (Ann. de Ch. et Ph. xv.), that 100 parts, by weight, of pure water consist of 11·1 of hydrogen and 88·9 oxygen, which is the ratio of 1 to 8·009, very nearly that of 1 to 8 above stated.

The processes for procuring a supply of hydrogen gas will now be intelligible. The first is the method by which Lavoisier made the analysis of water. It is founded on the fact that iron at a red heat decomposes water, the oxygen of that liquid uniting with the metal, and the hydrogen gas being set free. That the hydrogen which is evolved when zinc or iron is put into dilute sulphuric acid must be derived from the same source, is obvious from the consideration, that of the three substances, iron, sulphuric acid, and water, the last is the only one which contains hydrogen. The product of the operation, besides hydrogen, is sulphate of the protoxide of iron, if iron is used, or of the oxide of zinc, when zinc is employed, according to the following equation ; $HO + SO_3 + Fe = FeO + SO_3 + H$. The knowledge of the combining proportions of these substances will readily give the exact quantity of each product. These numbers are—

Water (8 oxy. + 1 hyd.)	9
Sulphuric Acid	40·1
Iron	28
Protoxide of Iron (28 iron + 8 oxygen) . . .	36
Sulphate of the Protoxide of Iron (40·1 + 36) . .	76·1

Hence for every 9 grains of water which are decomposed, 1 grain of hydrogen will be set free ; 8 grains of oxygen will unite with 28 grains of iron, forming 36 of the protoxide of iron; and the 36 grains of protoxide will combine with 40·1 grains of sulphuric acid, yielding 76·1 of sulphate of the protoxide of iron. A similar calculation may be employed when zinc is used, merely by substituting the equivalent of zinc (32·5) for that of iron. According to Mr. Cavendish, an ounce of zinc yields 676 cubic inches, and an equal quantity of iron 782 cubic inches of hydrogen gas.

The action of dilute sulphuric acid on metallic zinc affords an instance of what was once called *Disposing Affinity.* Zinc decomposes pure water at common temperatures with extreme slowness; but as soon as sulphuric acid is added, decomposition of the water takes place rapidly, though the acid merely unites with oxide of zinc. The former explanation was, that the affinity of the acid for oxide of zinc disposed the metal to unite with oxygen, and thus enabled it to decompose water; that is, the oxide of zinc was supposed to produce an effect previous to its existence. The obscurity of this explanation arises from regarding changes as consecutive, which are in reality simultaneous. There is no succession in the process; the oxide of zinc is not formed previously to its combination with the acid, but at the instant. There is, as it were, but one chemical change, which consists in the combination at one and the same moment of zinc with oxygen, and of oxide of zinc with the acid; and this change occurs because these two affinities, acting together, overcome the attraction of oxygen and hydrogen for one another.

(According to the views now most prevalent in regard to the nature of acids, it is not the water which is here decomposed, but the oil of vitriol or hydrated sulphuric acid, which contains hydrogen; its formula, according to the newer view, being H,SO_4, and on the older one, HO,SO_3. Taking the first of these two formulæ, the equation of the change is

$$Zn + H,SO_4 = H + Zn,SO_4\,;$$

and here there is no occasion for any such explanation as that above given. It is true that zinc does not decompose oil of vitriol until water be added, but that is because unless water be present the salt which is formed could not be dissolved, and its solution is necessary for the continuance of the action.)

Prop.—Transparent, colourless, inodorous, tasteless; powerful refractor of light; imperfect conductor of heat and electricity; very incompressible, its absolute diminution for a pressure of one atmosphere being only 51·3 millionths of its volume. (An. de Ch. et Ph. xxxvi. 140.) Its changes of form under varying temperatures have been already stated in the section on heat. Its sp. gr. is 1, being the unit to which the sp. gr. of all solids and liquids is referred as a convenient term of comparison. One cubic inch, at 62° and 30′ Bar., weighs 252·458 grains. It is 815 times heavier than atmospheric air. The sp. gr. of aqueous vapour is 0·6202, and 100 C. I. (containing 100 hydrogen and 50 oxygen), at 212° and 30′ Bar., weigh 14·96 grains; sp. gr. of ice is 0·92.

Owing partly to the extensive range of its own affinity, and partly to the nature of its elements, water is a chemical agent of great power. Of this, the preparation of hydrogen gas is an example; and indeed there are few complex changes, where oxygen and hydrogen are present, which do not give rise either to the production or decomposition of water. But, independently of the elements of which it is composed, it combines directly with many bodies. Sometimes it is contained in a variable ratio, as in ordinary solution; in other compounds it is present in a fixed definite proportion, as is exemplified by its union with several of the acids, the alkalies, and all salts that contain water of crystallization. These combinations are termed *hydrates.* Thus, concentrated sulphuric acid is a compound of one eq. of the real acid and one eq. of water; and its proper name is *hydrous sulphuric acid*, or *hydrate of sulphuric acid.* The prefix *hydro* has been sometimes used to signify the presence of water in definite proportion; but it is advisable, to prevent mistakes, to limit its employment to the compounds of hydrogen.

The purest water which can be found as a natural product, is procured by melting freshly fallen snow, or by receiving rain in clean vessels at a distance from houses. But this water is not absolutely pure; for if placed under the exhausted receiver of an air-pump, or boiled briskly for a few minutes, bubbles of gas escape from it. The air obtained in this way from snow water is much richer than atmospheric air in oxygen gas. According to Gay-Lussac and Humboldt it contains 34·8 per cent. of oxygen, and the air separated by ebullition from rain water contains 32 per cent. All water which has once fallen on the ground becomes impregnated with more or less earthy or saline matters, and can be separated from them only by distillation. The distilled water, thus obtained, and preserved in clean well-stopped bottles, is absolutely pure. Recently boiled water has the property of absorbing a portion of all gases, when its surface is in contact with them; and the absorption is promoted by brisk agitation. The following table, from Henry's Chemistry, shows the absorbability of different gases by water, deprived of all its air by ebullition.

100 C. I. water, at 60° and 30′ Bar., absorb of

	Dalton and Henry.	Saussure.
Sulphuretted Hydrogen	100 C. I.	253
Carbonic Acid	100	106
Nitrous Oxide	100	76
Olefiant Gas	12·5	15·3
Oxygen	3·7	6·5
Carbonic Oxide	1·56	6·2
Nitrogen	1·56	4·1
Hydrogen	1·56	4·6

The estimate of Saussure is in general too high. That of Dalton and Henry for nitrous oxide, according to the experiments of Davy, is considerably beyond the truth.

Its eq. is $= 9$; eq. vol. 100; symb. $H + O$, or HO, or $\dot{H}$, or aq. from aqua.

Peroxide or Binoxide.—Discovered by Thenard in 1818. Its preparation is founded on the fact that there are two oxides of barium, the peroxide and protoxide, the former of which is converted into the protoxide by the action of acids. When this process is conducted with the necessary precautions, the oxygen which is set free, instead of escaping in the form of gas, unites with the hydrogen of the water, and brings it to a maximum of oxidation. For a full detail of all the minutiæ of the process, the reader may consult the original memoir of Thenard;* the general directions are the following:—To six or seven ounces of water add so much pure concentrated hydrochloric acid as is sufficient to dissolve 230 grains of baryta; and after having placed the mixed fluids in a glass vessel surrounded with ice, add in successive portions 185 grains of peroxide of barium reduced to powder, and stir with a glass rod after each addition. When the solution, which takes place without effervescence, is complete, sulphuric acid is added in sufficient quantity for precipitating the whole of the baryta in the form of an insoluble sulphate, leaving the hydrochloric acid in solution. Another portion of peroxide of barium, amounting to 185 grains, is then put into the liquid: the free hydrochloric acid instantly acts upon it, and as soon as it is dissolved, the baryta is again separated as a sulphate by the addition of sulphuric acid. The solution is then filtered, in order to separate the insoluble sulphate of baryta; and fresh quantities of peroxide of barium are added in succession, till about three ounces have been employed. The liquid then contains from 25 to 30 times its volume of oxygen gas. The hydrochloric acid which has served to decompose the peroxide of barium during the whole process, is now removed by the cautious addition of sulphate of oxide of silver, and the sulphuric acid afterwards separated by solid baryta.

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* In the An. de Chim. et de Phys. vols. viii. ix. x. and l.; Annals of Philosophy, vols. xiii. and xiv.; and M. Thenard's Traité de Chimie.

A simpler process has lately been proposed by Pelouze. It consists in adding peroxide of barium to diluted hydrofluoric acid in a silver or platinum vessel as long as it is decomposed. The fluoride of barium, which is formed, being insoluble, is deposited and separated by filtration or subsidence. The liquid then contains nothing but water and peroxide of hydrogen, and is to be treated as follows.

Peroxide of hydrogen, as thus prepared, is still diluted with a considerable quantity of water. To separate the latter, the mixed liquids are placed, with a vessel of strong sulphuric acid, under the exhausted receiver of an air-pump. As the water evaporates, the density of the residue increases, till at last it acquires the sp. gr. of 1·452. The concentration cannot be pushed further; for if kept under the receiver after reaching this point, the peroxide itself gradually but slowly volatilizes without change.

Prop.—A colourless transparent liquid, inodorous, and of a metallic taste; volatilizes *in vacuo* less rapidly than water; retains its liquid form at all degrees of cold to which it has been exposed; at 59° is resolved into oxygen and water, and hence should be always kept in glass tubes surrounded by ice. It mixes with water in all proportions; bleaches litmus and turmeric paper, whitens the skin and tongue, causing to both a pricking sensation, and thickens the saliva. The most remarkable of its properties is its facility of decomposition. Diffused daylight does not seem to exert any influence over it, and even the direct solar rays act upon it tardily. It effervesces from escape of oxygen at 59°, and the sudden application of a higher temperature, as that of 212°, gives rise to such rapid evolution of gas as to cause an explosion. Water, apparently by combining with the peroxide, renders it more permanent; but no degree of dilution can enable it to bear the heat of boiling water, at which temperature it is entirely decomposed. All the metals except iron, tin, antimony, and tellurium, have a tendency to decompose it, converting it into oxygen and water. A state of minute mechanical division is essential for producing rapid decomposition. If the metal is in mass, and the peroxide diluted with water, the action is slow. The metals which have a strong affinity for oxygen are oxidized at the same time, such as potassium, sodium, arsenic, molybdenum, manganese, zinc, tungsten, and chromium; while others, such as gold, silver, platinum, iridium, osmium, rhodium, palladium, and mercury, retain the metallic state.

It is decomposed at common temperatures by many of the metallic oxides. That some protoxides should have this effect, would be anticipated in consequence of their tendency to pass into a higher state of oxidation. The protoxides of iron, manganese, tin, cobalt, and others, act on this principle, and are really converted into peroxides. The peroxides of barium, strontium, and calcium may likewise be formed by the action of peroxide of hydrogen on baryta, strontia, and lime. But it is a singular fact, of which no satisfactory explanation has been given, that some oxides decompose it without passing into a higher degree of oxidation. The peroxides of lead, mercury, gold, platinum, manganese, and cobalt possess this property in the greatest perfection, acting on peroxide of hydrogen, when concentrated, with surprising energy. The decomposition is complete and instantaneous; oxygen gas is evolved so rapidly as to produce a kind of explosion; and such intense temperature is excited, that the glass tube in which the experiment is conducted becomes red-hot. The reaction is very great, even when the peroxide of hydrogen is diluted with water. Oxide of silver occasions very perceptible effervescence when put into water which contains only 1-50th of its bulk of oxygen. All the metallic oxides, which are decomposed by a red heat, such as those of gold, platinum, silver, and mercury, are reduced to the metallic state when they act upon peroxide of hydrogen. This effect cannot be altogether ascribed to heat disengaged during the action; for oxide of silver suffers reduction when put into a very dilute solution of the peroxide, although the decomposition is not then attended by an appreciable rise of temperature.

While the tendency of metals and metallic oxides is to decompose the peroxide of hydrogen, acids have the property of rendering it more stable. In proof of this, let a portion of that liquid, somewhat diluted with water, be heated till it begins to effervesce from the escape of oxygen gas; let some strong acid, as the nitric, sulphuric, or hydrochloric, be then dropped into it, and the effervescence will cease on the instant. When a little finely divided gold is put into a weak solution of peroxide of hydrogen, containing only 10, 20, or 30 times its bulk of oxygen, brisk effervescence ensues; but on letting one drop of sulphuric acid fall into it, effervescence ceases instantly; it is reproduced by the addition of potassa, and is again arrested by adding a second portion of acid. The only acids that do not possess this property are those that have a low degree of acidity, as carbonic and boracic acids; or those which suffer a chemical change when mixed with the peroxide of hydrogen, such as hydriodic, hydrosulphuric, and sulphurous acids. Acids appear to increase the stability of the peroxide in the same way as water does, namely, by combining chemically with it. Several compounds of this kind were formed by Thenard, before he was aware of the existence of the peroxide of hydrogen. They were made by dissolving peroxide of barium in some dilute acid, such as the nitric, and then precipitating the baryta by sulphuric acid. As nitric acid was supposed under these circumstances to combine with an additional quantity of oxygen, Thenard applied the term oxygenized nitric acid to the resulting compound, and described several other new acids under a similar title. But the subsequent discovery of peroxide of hydrogen put the nature of the oxygenized acids in a clearer light; for their properties are easily explicable on the supposition that they are composed, not of acids and oxygen gas, but of acids united with peroxide of hydrogen.

Peroxide of hydrogen was analysed by diluting a known weight of it with water, and then decomposing it by boiling the solution.

Its eq. is = 17; symb. $H + 2O$, or HO_2, or $\ddot{H}$.

SECTION V.

NITROGEN.

Hist.—First noticed by Rutherford of Edinburgh in 1772. Discovered to be a constituent of the atmosphere by Lavoisier in 1775, and by Scheele about the same time. It was termed azote (*α* privative, and *ζωη life*) by Lavoisier, from its inability to support respiration. The name of nitrogen is derived from its being an element of nitric acid.

Prep.—1. By burning a piece of phosphorus in a jar full of air inverted over water. The strong affinity of phosphorus for oxygen enables it to burn till the whole of that gas is consumed. The product of the combustion, metaphosphoric acid, is at first diffused through the residue in the form of a white cloud; but as this substance is rapidly absorbed by water, it disappears entirely in the course of half an hour. The residual gas is nitrogen, containing a small quantity of carbonic acid and vapour of phosphorus, both of which may be removed by agitating it briskly with a solution of pure potassa. Several other substances may be employed for withdrawing oxygen from atmospheric air. A solution of protosulphate of iron, charged with binoxide of nitrogen, absorbs the oxygen in the space of a few minutes. A stick of phosphorus produces the same effect in twenty-four hours, if exposed to a temperature of 60°. A solution of sulphuret of potassium or calcium acts in a similar manner; and a mixture of equal parts of iron filings and sulphur, made into a paste with water, may be employed with the same intention. Both these processes, however, are inconvenient from their slowness.—2. By exposing a mixture of fresh muscle and nitric acid of sp. gr. 1·20 to a moderate temperature. Effervescence then takes place, and a large quantity of gaseous matter is evolved, which is nitrogen mixed with a little carbonic acid. The latter must be removed by agitation with lime water; but the residue still retains a peculiar odour, indicative of the presence of some volatile principle which cannot be wholly separated from it. The theory of this process is somewhat complex, and is not yet fully understood. 3. By transmitting chlorine gas through a solution of ammonia, when that alkali yields its hydrogen to the chlorine, and its nitrogen is evolved.

Prop.—Colourless, tasteless, inodorous; always gaseous when uncombined; sp. gr. 0·9722, so that 100 C. I. weigh 30·166 grains; no action on the blue colour of plants; water dissolves 1½ per cent. It is distinguished from other gases more by negative characters than by any striking quality. It is not a supporter of combustion; but, on the contrary, extinguishes all burning bodies that are immersed in it. No animal can live in it; but yet it exerts no injurious action either on the lungs or on the system at large, the privation of oxygen gas being the sole cause of death. It is not inflammable like hydrogen; though, under favourable circumstances, it may be made to unite with oxygen.

Considerable doubt exists as to the nature of nitrogen. Though ranked among the simple non-metallic bodies, some circumstances have led to the suspicion that it is compound; and this opinion has been warmly advocated by Davy and Berzelius. The chief argument in favour of this view is drawn from the phenomena that attend the formation of what is called the *ammoniacal amalgam.* From the metallic appearance of this substance, it was supposed to be a compound of mercury and a metal ; and as the only method of forming it is by the action of galvanism on a salt of ammonia, in contact with a globule of mercury, it follows that the metal, if present at all, must have been supplied by the ammonia. Now ammonia is composed of hydrogen and nitrogen; and as the former, from its small sp. gravity, can hardly be supposed to contain a metal, it was inferred that it must be present in the latter. Unfortunately for this argument, the supposed metal cannot be obtained in a separate state. The amalgam no sooner ceases to be under galvanic influence than its elements begin to separate spontaneously, and in a few minutes decomposition is complete, the sole products being ammonia, hydrogen, and pure mercury. Davy accounted for this change on the supposition that water is decomposed; that its oxygen reproduces nitrogen by uniting with the supposed metal; and that one part of its hydrogen forms ammonia by uniting with the nitrogen, while the remainder escapes in the form of gas. But Gay-Lussac and Thenard (Recherches Physico-Chimiques, vol. i.) declare that the amalgam resolves itself into mercury, ammonia, and hydrogen, even though perfectly free from moisture; and they infer from their experiments that it is composed of those three substances combined directly with each other. It hence appears that the examination of the ammoniacal amalgam affords no proof of the compound nature of nitrogen; nor was Davy's attempt to decompose that gas by aid of potassium, intensely heated by a galvanic current, attended with better success.

Its eq. is 14·15; eq. vol. = 100; symb. N.

The compounds of nitrogen treated of in this section are the following, exclusive of atmospheric air, which is regarded as a mechanical mixture:—

	By Volume.			By Weight.			
	Nit.		Oxy.	Nit.	Oxy.	Equiv.	Formulæ.
Nitrous Oxide	100	.	50	14·15	+8	= 22·15	$N+O$
Nitric Oxide	100	.	100	14·15	+16	= 30·15	$N+2O$
Hyponitrous Acid	100	.	150	14·15	+24	= 38·15	$N+3O$
Nitrous Acid	100	.	200	14·15	+32	= 46·15	$N+4O$
Nitric Acid	100	.	250	14·15	+40	= 44·15	$N+5O$

ON THE ATMOSPHERE.

The earth is everywhere surrounded by a mass of gaseous matter called the atmosphere, which is preserved at its surface by the force of gravity, and revolves together with it around the sun. It is colourless and invisible, excites neither taste nor smell when pure, and is not sensible to the touch unless when it is in motion. It possesses the physical properties of elastic fluids in a high degree. Its sp. gr. is unity, being the standard with which the density of all gaseous substances is compared. At 30′ Bar. and 32° it is 769·4 times lighter than water, and 10462 than mercury; or at 62°, 815 times lighter than water, and nearly 11065 times lighter than mercury. The knowledge of its exact weight is an essential element in many physical and chemical researches, and has been determined with very great care by Prout, who finds that 100 C. I. of pure and dry atmospheric air, at 60° and 30′ Bar. weigh 31·0117 grains.

The pressure of the atmosphere was first noticed early in the 17th century by Galileo, and was afterwards demonstrated by his pupil Torricelli, to whom science is indebted for the invention of the barometer. Its pressure at the level of the sea is equal to a weight of about 15 pounds on every square inch of surface, and is capable of supporting a column of water 34 feet high, and one of mercury of 30 inches; that is, a column of mercury of one inch square and 30 inches long has the same weight (nearly 15 pounds) as a column of water of equal base and 34 feet long, and as a column of air of equal base reaching from the level of the sea to the extreme limit of the atmosphere. By the use of the barometer it was discovered that the atmospheric pressure is variable. It varies according to the elevation above the level of the sea, and on this principle the height of mountains is estimated. Supposing the density of the atmosphere to be uniform, a fall of one inch in the barometer would correspond to 11065 inches, or 922 feet of air; but in order to make the calculation with accuracy, allowance must be made for the increasing rarity of the air, and for various other circumstances which are detailed in works on meteorology. (Daniel's Meteorological Essays, 2nd edit., 376.) From causes at present not understood, the pressure varies likewise at the same place. On this depend the indications of the barometer as a weather-glass; for observation has fully proved, that the weather is commonly fair and calm when the barometer is high, and usually wet and stormy when the mercury falls.

Atmospheric air is highly compressible and elastic, so that its particles admit of being approximated to a great extent by compression, and expand to an extreme degree of rarity, when the tendency of its particles to separate is not restrained by external force. The volume of air and all other gaseous fluids, so long as they retain the elastic state, is inversely as the pressure to which they are exposed. Thus a portion of air which occupies 100 measures when compressed by a force of one pound, will be diminished to fifty measures when the pressure is doubled, and will expand to 200 measures when the compression is equal to half a pound. This law was first demonstrated in 1662 by the celebrated Boyle, and a second demonstration of it was given some years afterwards by the French philosopher Mariotte, apparently without being aware that the discovery had been previously made in England. It is hence frequently called the law of Mariotte. Till lately it had not been verified for very great pressures; but from the experiments of Oersted in 1825, who extended his observations to air compressed by a force equal to 110 atmospheres, it may be inferred to be quite general, except when the gaseous matter assumes the liquid form. (Ed. Journal of Science, iv. 224.) Gases vary from this law when they approach the point at which they assume the liquid form. At what pressure air becomes liquid is uncertain, since all attempts to condense it have hitherto been unsuccessful.

The extreme compressibility and elasticity of the air accounts for the facility with which it is set in motion, and the velocity with which it is capable of moving. It is subject to the laws which characterize elastic fluids in general. It presses, therefore, equally on every side;

and when some parts of it become lighter than the surrounding portions, the denser particles rush rapidly into their place and force the more rarified ones to ascend. The motion of air gives rise to various familiar phenomena. A stream or current of air is wind, and an undulating vibration excites the sensation of sound.

The atmosphere is not of equal density at all its parts. This is obvious from the consideration that those portions which are next the earth sustain the whole pressure of the atmosphere, while the higher strata bear only a part. The atmospheric column diminishes in length as the distance from the earth's surface increases; and, consequently, the greater the elevation the lighter must be the air. It is not known to what height the atmosphere extends. From calculations founded on the phenomena of refraction, its height is supposed to be about 45 miles; and Wollaston estimated, from the law of expansion of gases, that it must extend to at least 40 miles with properties unimpaired by rarefaction. In speculating on its extent beyond that distance, it becomes a question whether the atmosphere is or is not limited to the earth. This subject was discussed with his usual sagacity by Wollaston, in an Essay on the Finite Extent of the Atmosphere (Phil. Trans., 1822). Supposing the atmosphere unlimited, it should pervade all space, and accumulate about the sun, moon, and planets, forming around each an atmosphere, the density of which would depend on their respective forces of attraction. Now Wollaston inferred from astronomical observations made by himself and Kater, that there is no solar atmosphere; and the observations of other astronomers appear to justify the same inference with respect to the planet Jupiter. If the accuracy of these conclusions be admitted, it follows that our atmosphere is confined to the earth; and it may next be asked, by what means is its extent limited? Wollaston accounted for it by supposing the air, after attaining a certain degree of rarefaction, to possess such feeble elasticity, that the tendency of its particles to separate further from each other is counteracted by gravity. The unknown height at which this equilibrium between the two forces of elasticity and gravitation takes place, is the extreme limit of the atmosphere. The loss of elasticity may be ascribed to two powerful and concurring causes; namely, to the distance between the particles of air when highly rarefied, and to the extreme cold which prevails in the higher strata of the atmosphere.

The temperature of the atmosphere varies with its elevation. Gaseous fluids permit radiant matter to pass freely through them without any absorption, and therefore without their temperature being influenced by its passage. The atmosphere is not heated by transmitting the rays of the sun, but receives its heat solely from the earth, and chiefly by actual contact; so that its temperature becomes progressively lower as the distance from the general mass of the earth increases. Another circumstance which contributes to the same effect, is the increasing tenuity of the atmosphere; for the temperature of rarefied air is less raised by a given quantity of heat, than that of the same portion of air when compressed, owing to its sp. heat being greater in the former state than in the latter. From the joint influence of both these causes, it is found, that, in ascending into the atmosphere, the temperature diminishes at the rate of one degree for about every 352 feet. The rate of decrease is probably much slower at considerable distances from the earth; but still there is no reason to doubt that the temperature continues to decrease with the increasing elevation. There must consequently, in every latitude, be a point where the thermometer never rises above 32°, and where ice is never liquefied. This point varies with the latitude, being highest within the tropics, and descending gradually as we advance towards the poles. The following table, from the Supplement to the Encyclopedia Britannica, page 190, article Climate, shows the point of perpetual ice corresponding to different latitudes:—

Latitude.	English Feet in Height.	Latitude.	English Feet in Height.
0°	15,207	45°	7,671
5°	15,095	50°	6,334
10°	14,764	55°	5,034
15°	14,220	60°	3,818
20°	13,478	65°	2,722
25°	12,557	70°	1,778
30°	11,484	75°	1,016
35°	10,287	80°	453
40°	9,001	85°	117

Air was one of the four elements of the ancient philosophers, and their opinion of its nature prevailed generally, till its accuracy was rendered questionable by the experiments of Boyle, Hooke, and Mayow. The discovery of oxygen gas in 1774 paved the way to the knowledge of its real composition, which was discovered about the same time by Scheele and Lavoisier. The former exposed some atmospheric air to a solution of sulphuret of potassium, which gradually absorbed the whole of the oxygen. Lavoisier effected the same object by the combustion of iron wire and phosphorus.

The earlier analyses of the air did not agree very well with each other. According to the researches of Lavoisier, it is composed of 27 measures of oxygen and 73 of nitrogen. The analysis of Scheele gave a somewhat higher proportion of oxygen. Priestley found that the quantity of oxygen varies from 20 to 25 per cent.; and Cavendish estimated it at only 20. These discrepancies must have arisen from imperfections in the mode of analysis; for the proportion of oxygen has been found by subsequent experiments to be almost, if not exactly, that which was stated by Cavendish. The results of Scheele and Priestley are clearly referrible to this cause. It is now known that the processes they employed cannot be relied on, unless certain precautions are taken of which those chemists were ignorant. Recently boiled water absorbs nitrogen; and, consequently, if sulphuret of potassium be dissolved in that liquid by the aid of heat, the solution, when agitated with air, takes up a portion of nitrogen, and thereby renders the apparent absorption of oxygen too great. This inconvenience may be avoided by dissolving the sulphuret in cold unboiled water. Binoxide of nitrogen, employed by Priestley, removes all the oxygen in the course of a few seconds; but, for reasons which will soon be mentioned, its indications are apt to be fallacious. The combustion of phosphorus, as well as the gradual oxidation of that substance, acts in a very uniform manner, and removes the whole of the oxygen completely. The residual nitrogen contains a little of the vapour of phosphorus, which increases the bulk of that gas by 1-40th, for which an allowance must be made in estimating the real quantity of nitrogen.

Since chemists have learned the precautions to be taken in the analysis of the air, a close correspondence has been observed in the results of their experiments upon it. The researches of Davy, Dalton, Gay-Lussac, Thomson, and others, leave no doubt that 100 measures of pure atmospheric air consist of 20 or 21 volumes of oxygen, and 80 or 79 of nitrogen. The most approved mode of analysis consists in mixing with the air a quantity of hydrogen sufficient to convert all the oxygen present into water, and kindling the mixture by the electric spark. The combination may also be effected without detonation by means of spongy platinum. Water is formed, and is condensed; and since that liquid is composed of one volume of oxygen and two of hydrogen, one-third of the diminution must give the exact quantity of oxygen. This process is so easy of execution, and so uniform in its indications, that it is now employed nearly to the total exclusion of all others.

Such is the constitution of pure atmospheric air. But the atmosphere is never absolutely pure; for it always contains a certain variable quantity of carbonic acid and watery vapour, besides the odoriferous matter of flowers and other volatile substances, which are also frequently present. Saussure found carbonic acid in air collected at the top of Mont Blanc; and it exists at all altitudes which have been hitherto attained. Saussure, in a recent essay, states the proportion of this gas to vary at the same place within short intervals of time. It is greater in summer than in winter; and from observations made during spring, summer, and autumn, in the open fields, and in calm weather, its proportion is inferred to be always greater at night than in the day, and to be more abundant in gloomy than in bright weather. A very moist state of the ground, as after much rain, diminishes the quantity of carbonic acid, apparently by direct absorption. It is rather more abundant in elevated situations, as on the summits of high mountains, than in the plains; but its quantity is there nearly the same in day and night, in wet and dry weather, because the higher strata of the air are less influenced by vegetation and the state of the soil. Saussure thinks also that a highly electrical state of the atmosphere tends to diminish the quantity of carbonic acid. He found that 10,000 parts of air contain 4·9 of carbonic acid as a mean, 6·2 as a maximum, and 3·7 as a minimum. (An. de Ch. et Ph. xxxviii. 411, xliv. 5.)

Another substance which is always present in the atmosphere is ammonia. This has been demonstrated by Liebig. The ammonia is derived from the putrefaction and decay of animal and vegetable matter, and although its quantity is very small in proportion to the mass of the atmosphere, yet it is always sufficient for the wants of growing vegetables, which obtain all or nearly all the nitrogen they contain from the ammonia present in the atmosphere, and after death restore it again, to serve as food for new generations of plants, and through plants of animals also. Although the proportion of ammonia in the atmosphere is so small that we cannot detect it in any given portion of air, still there can be no doubt of its presence, when we reflect that every decaying plant or animal sends the whole of its nitrogen into the atmosphere in the form of ammonia.

Moreover, Liebig has shown that it is quite easy to detect the presence of ammonia in the atmosphere by looking for it in rain-water, which, in passing through the air, absorbs all the ammonia it meets with. According to his experiments, rain-water invariably contains ammonia (in the form of carbonate), to which are owing some of its properties, as for example its superior softness. By adding a few drops of diluted sulphuric acid to a gallon of rain water, and concentrating to a small volume, the ammonia present is accumulated; and on adding lime or potash to the residue of the evaporation, the ammonia is given off, and may easily be recognized by its smell. Liebig states, and correctly, that the ammonia thus obtained has not the pure smell of the gas, but a putrid offensive smell along with it, which is a very significant mark of its origin, being, as above stated, derived from putrefying organic matters. The proportion of ammonia in rain-water is greatest in the first shower after long drought, and least after continued rains, for obvious reasons. There is little doubt also that the nitric acid sometimes observed in rain-water after thunder-storms, as well as that formed in nitrification, are derived from the ammonia in the atmosphere.

The chief chemical properties of the atmosphere are owing to the presence of oxygen gas. Air from which this principle has been withdrawn is nearly inert. It can no longer support respiration and combustion, and metals are not oxidized by being heated in it. Most of the spontaneous changes which mineral and dead organized matters undergo, are owing to the powerful affinities of oxygen. The uses of the nitrogen are in a great measure unknown. It was supposed to act as a mere diluent to the oxygen; but it most probably serves some other useful purpose in the economy of animals, the exact nature of which has not been discovered.

The knowledge of the composition of the air, and of the importance of oxygen to the life of animals, naturally gave rise to the notion that the healthiness of the air at different times, and in different places, depends on the relative quantity of this gas. It was therefore supposed that the purity of the atmosphere, or its fitness for communicating health and vigour, might be discovered by determining the proportion of oxygen; and hence the origin of the term *Eudiometer*, which was applied to the apparatus for analyzing the air. But this opinion, though at first supported by the discordant results of the earlier analysts, was soon proved to be fallacious. On the contrary, the composition of the air is not only constant in the same place, but is the same in all regions of the earth, and at all altitudes. Air collected at the summit of the highest mountains, such as Mont Blanc and Chimborazo, contains the same proportion of oxygen as that of the lowest valleys. The air of Egypt was found by Berthollet to be similar to that of France. The air which Gay-Lussac brought from an altitude of 21,735 feet above the earth, had the same composition as that collected at a short distance from its surface. Even the miasms of marshes, and the effluvia of infected places, owe their noxious qualities to some principle of too subtile a nature to be detected by chemical means, and not a to deficiency of oxygen. Seguin examined the infectious atmosphere of an hospital, the odour of which was almost intolerable, and could discover no appreciable deficiency of oxygen, or other peculiarity of composition.

The question has been much discussed, whether the oxygen and nitrogen gases of the atmosphere are simply intermixed, or chemically combined with each other. Appearances are at first view greatly in favour of the latter opinion. Oxygen and nitrogen gases differ in density, and therefore it might be expected, were they merely mixed together, that the oxygen as the heavier gas ought, in obedience to the force of gravity, to collect in the lower regions of the air, while the nitrogen should have a tendency to occupy the higher. But this has nowhere been observed. If air be confined in a long tube preserved at perfect rest, its upper part will contain just as much oxygen as the lower, even after an interval of many months; nay, if the lower part of it be filled with oxygen, and the upper with nitrogen, these gases will be found in the course of a few hours to have mixed intimately with one another. The constituents of the air are, also, in the exact proportion for combining. By measure they are nearly in the simple ratio of 1 to 4, which agrees with the law of combination by volume; and by weight they are as 8 to 28, which corresponds to 1 eq. of oxygen and 2 of nitrogen.

Strong as are these arguments in favour of the chemical theory, it is nevertheless liable to objections which appear insuperable. The atmosphere possesses all the characters that should arise from a mechanical mixture. There is not, as in all other cases of chemical union, any change in the bulk, form, or other qualities of its elements. The nitrogen manifests no attraction for the oxygen. All bodies which have an affinity for oxygen abstract it from the atmosphere with as much facility as if the nitrogen were absent altogether. Even water effects this separation; for the air which is expelled from rain-water by ebullition contains more than 21 per cent. of oxygen. When oxygen and nitrogen gases are mixed together in the ratio of 1 to 4, the mixture occupies precisely 5 volumes, and has every property of pure atmospheric air. The refractive power of the atmosphere is precisely such as a mixture of oxygen and nitrogen gases ought to possess, and different from what would be expected were its elements chemically united. (Edinburgh Journal of Science, iv. 211.)

Since the elements of the air cannot be regarded as in a state of actual combination, it is necessary to account for the steadiness of their proportion on some other principle. It has been conceived that the affinity of oxygen and nitrogen for one another, though insufficient to cause their combination when mixed together at ordinary temperatures, might still operate in such a manner as to prevent their separation; that a certain degree of attraction is even then exerted between them, which is able to counteract the tendency of gravity. An opinion of this kind was advanced by Berthollet, in his *Statique Chimique*, and defended by Murray. This doctrine, however, is not satisfactory. It is conceivable that oxygen and nitrogen may attract each other in the way supposed; and it may be admitted that this supposition explains why these two gases continue in a state of perfect mixture. But still the explanation is unsatisfactory; and for the following reason:—Dalton took two cylindrical vessels, one of which was filled with carbonic acid, the other with hydrogen gas; the latter was placed perpendicularly over the other, and a communication was established between them. In the course of a few hours hydrogen was detected in the lower vessel, and carbonic acid gas in the upper. If the upper vessel be filled with oxygen, nitrogen, or any other gas, the same phenomena will ensue: the gases will be found, after a short interval, to be in a state of mixture, and will at last be distributed equally through both vessels. Now this result cannot be ascribed to the action of affinity. Carbonic acid cannot be made to unite either with hydrogen, oxygen, or nitrogen; and therefore, it is gratuitous to assert that it has an affinity for them. Some other power must be in operation, capable of producing the mixture of gases with each other, independently of chemical attraction; and if this power can cause carbonic acid to ascend through a gas which is twenty-two times lighter than itself, it will surely explain why oxygen and nitrogen gases, the densities of which differ so little, should be intermingled in the atmosphere.

The explanation which Dalton has given of these phenomena is founded on the assumption, that the particles of one gas, though highly repulsive to each other, do not repel those of a different kind. Hence one gas should act as a vacuum with respect to another; and if a vessel full of carbonic acid communicate with another of hydrogen, the particles of each gas should insinuate themselves between the particles of the other till they are equally diffused through both vessels. The particles of the carbonic acid do not indeed fill the space occupied by the hydrogen with the same velocity as if it were a real vacuum, because the particles of the hydrogen afford a mechanical impediment to their progress. The ultimate effect, however, is the same as if the vessel of hydrogen had been a vacuum. (Manchester Memoirs, vol. v.)

Though it would not be difficult to find objections to this hypothesis, it has the merit of being applicable to every possible case; which cannot, I conceive, be admitted of the other. It accounts not only for the mixture of gases, but for the equable diffusion of vapours through gases, and through each other. This view receives support from Graham's experiments on the diffusion of gases. (Phil. Trans. Edin. 1831.) When a gas is contained in a glass bell jar which has a crack or fissure in its sides, or communicates with the air by a narrow aperture, or is contained in a porous vessel, the gas gradually diffuses itself into the air, and air into the gas, each passing through the chink or other small opening at the same time, but in opposite directions. On ascertaining after an interval how much gas has escaped from, and how much air entered into, the vessel, it will be found that the respective quantities depend on the relative sp. gravities; and the same principle of intermixture equally applies when the apertures of communication are large, as when they are small. Each gas has a diffusiveness peculiar to itself, and which is greater as its sp. gr. is less. Graham determined the rate of diffusion for different gases by means of what he calls a *diffusion tube*, which is simply a graduated tube closed at one end by plaster of Paris, a substance, when moderately dry, possessed of the requisite porosity. He has been led by direct experiment to the following conclusion: that "the diffusion or spontaneous intermixture of two gases in contact, is effected by an interchange in position of indefinitely small volumes of the gases, which gases are not necessarily of equal magnitude, being, in the case of each gas, inversely proportional to the square root of the density of that gas." The relative diffusiveness of each gas may hence be represented by the reciprocal of the square root of its sp. gr. Thus, the sp. gr. of air being 1, its diffusiveness is 1 also; that of hydrogen is

$$\frac{1}{\sqrt{0{\cdot}069}} = \frac{1}{0{\cdot}2627} = 3{\cdot}807\text{; that of oxygen } \frac{1}{\sqrt{1{\cdot}102}} = \frac{1}{1{\cdot}05} = 0{\cdot}9524\text{;}$$

$$\text{and that of nitrogen } \frac{1}{\sqrt{0{\cdot}972}} = 1{\cdot}014\text{;}$$

so that the relative power of diffusion of air, hydrogen, oxygen, and nitrogen is indicated by the numbers, 1, 3·807, 0·9524 and 1·014. In gases which are very sparingly soluble in water, and hence not condensable by the moisture of the plaster of Paris, the results of experiment coincide so exactly with the law, that Graham suggests its application to determine the sp. gr. of gases. Thus if g denote the diffusiveness of a gas, as found by careful experiment, and d its sp. gr.; then, since, by the law of diffusion,

$$g = \frac{1}{\sqrt{d}}\text{, we have } d = \frac{1}{g^{2}}.$$

It is obvious that these phenomena cannot be referred to any chemical principle, but are dependent on the mechanical constitution of gases. It has been shown, in a very clever paper by T. Thomson of Clitheroe (Phil. Mag., 3rd Series, iv. 321), that the law of gaseous diffusion is included under Dalton's hypothesis, that one gas is as a vacuum with respect to another. For it is a law deduced from the physical properties of gaseous bodies, that the velocities of gases flowing under like circumstances into a vacuum are inversely as the square roots of their sp. gravities, which is precisely the same law that regulates their flow into each other.

There is still one circumstance for consideration respecting the atmosphere. Since oxygen is necessary to combustion, to the respiration of animals, and to various other natural operations, by all of which that gas is withdrawn from the air, it is obvious that its quantity would gradually diminish unless the tendency of those causes were counteracted by some compensating process. To all appearance there does exist some source of compensation; for chemists have not hitherto noticed any change in the constitution of the atmosphere. The only source by which oxygen is known to be supplied, is the action of growing vegetables. A healthy plant absorbs carbonic acid during the day, appropriates the carbon of that gas to its own wants, and evolves the oxygen with which it was combined. During the night, indeed, an opposite effect is produced. Oxygen gas then disappears, and carbonic acid is given out; but it follows from the experiments of Priestley, Davy, and Daubeny, that plants during 24 hours yield more oxygen than they consume. Whether living vegetables make a full compensation for the oxygen removed from the air by the processes above mentioned, is uncertain. From the great extent of the atmosphere, and the continual agitation to which its different parts are subject by the action of winds, the effects of any deteriorating process would be very gradual, and a change in the proportion of its elements could be perceived only by observations made at very distant intervals; but all the existing evidence is in favour of the opinion that an entire compensation is effected.

Besides oxygen, nitrogen, carbonic acid, ammonia, and traces of volatile organic substances, air, as already stated, always contains a greater or less amount of the vapour of water. The methods and instruments employed for determining its quantity have been described in the article Evaporation. As these instruments are termed hygrometers, the moisture of the atmosphere is often called hygrometric; and solid substances which absorb it are said to contain hygrometric water.

PROTOXIDE OF NITROGEN.

Hist.—Dephlogisticated air of Priestley, its discoverer; and the nitrous oxide of Davy, who studied it minutely. (Researches on the Nitrous Oxide, 1800.)

Prep.—It may be formed by exposing nitric oxide for some days to the action of iron filings, or other substances which have a strong affinity for oxygen, when the nitric oxide loses one-half of its oxygen, and is converted into the protoxide; but the most convenient method is by nitrate of ammonia. This salt is prepared by neutralizing with carbonate of ammonia pure nitric acid diluted with about three parts of water, and concentrating by evaporation until a drop of the liquid let fall on a cold plate becomes a firm mass, adding a little ammonia towards the close to ensure neutrality. The salt after cooling is broken to pieces, introduced into a retort, and heated by a lamp or pan of charcoal: at first, below 400°, fusion ensues; and as the heat rises to 480° or 500°, rapid decomposition sets in, which continues until all the salt disappears. If a white cloud appears within the retort, due to some of the salt subliming undecomposed, the heat should be checked.

The sole products of this operation, when carefully conducted, are water and protoxide of nitrogen. The nature of the change will be readily understood by comparing the composition of nitrate of ammonia with that of the products derived from it. These, in round numbers, are as follows:—

Nitric Acid.	Ammonia.	Water.	Prot. of Nitrogen.
Nitrogen 14 or 1 eq.	Nitrogen 14 or 1 eq.	Hyd. 3 or 3 eq.	Nit. 28 or 2 eq.
Oxygen 40 or 5 eq.	Hydrogen 3 or 3 eq.	Oxy. 24 or 3 eq.	Oxy. 16 or 2 eq.
54	17	27	44

The same expressed in symbols is

$$NH_3 + NO_5 = 3HO + 2NO.$$

It thus appears that the hydrogen in the ammonia takes so much oxygen as is sufficient for forming water, and the residual oxygen converts the nitrogen both of the nitric acid and of the ammonia into protoxide of nitrogen: 71 grains of the salt will thus yield 44 grains of protoxide of nitrogen and 27 of water.

Prop.—Colourless, slightly agreeable odour, and sweetish taste; commonly gaseous, but at 45° and under a pressure of 50 atmospheres it is liquid; sp. gr. of the gas = 1·5241, and 100 C. I. weigh 47·22 grains; no action on test paper. Recently boiled water at 60° dissolves nearly its own volume of the gas, and yields it unchanged by boiling: hence it cannot be preserved over cold water, and may by it be separated from gases which are insoluble in water. It is a supporter of combustion. Most substances burn in it with far greater energy than in the atmosphere. When a recently extinguished candle with a very red wick is introduced into it, the flame is instantly restored. Phosphorus, if previously kindled, burns in it with great brilliancy. Sulphur, when burning feebly, is extinguished by it; but if immersed while the combustion is lively, the size of the flame is considerably increased. With an equal bulk of hydrogen it forms a mixture which explodes violently by the electric spark or by flame. In all these cases the product of combustion is the same as when oxygen gas or atmospheric air is used. The protoxide is decomposed; the combustible matter unites with its oxygen, and the nitrogen is set free. It suffers decomposition when a succession of electric sparks is passed through it, and a similar effect is caused by conducting it through a porcelain tube heated to incandescence. It is resolved, in both instances, into nitrogen, oxygen, and nitrous acid.

Davy discovered that it may be taken into the lungs with safety, and that it supports respiration for a few minutes. He breathed 9 quarts of it, contained in a silk bag, for three minutes, and 12 quarts for rather more than four; but no quantity could enable him to bear the privation of atmospheric air for a longer period. Its action on the system, when inspired, is very remarkable. A few deep inspirations are followed by most agreeable feelings of excitement, similar to the earlier stages of intoxication. This is shewn by a strong propensity to laughter, by a rapid flow of vivid ideas, and an unusual disposition to muscular exertion. These feelings, however, soon subside; and the person returns to his usual state without experiencing the languor or depression which so universally follows intoxication from spirituous liquors. Its effects, however, on different persons, are various; and in individuals of a plethoric habit it sometimes produces giddiness, headache, and other disagreeable symptoms.

When 100 measures of it are mixed with 100 of hydrogen and fired by electricity, 100 of nitrogen gas remain, and the sole other product is water. As 100 of hydrogen unite with 50 of oxygen, to form water, it follows that 100 measures of the protoxide contain 100 of nitrogen and 50 of oxygen gases. This result, obtained by Davy, has been confirmed by Henry, who analyzed it by means of carbonic oxide gas (An. Phil., N. S., viii. 299). Now,

100 cubic inches of nitrogen gas weigh . .	30·166 grains
50 do. oxygen	17·054
These numbers added together amount to . .	47·220

which must be the weight of 100 C. I. of the protoxide. Its composition by weight is determined by the same data, being 17·054 oxygen to 30·166 nitrogen, or 8 to 14 nearly, as already stated. Its eq. is = 22·15; eq. vol. = 100; symb. $N + O$, NO, or N.

Faraday has lately succeeded in solidifying this gas, and is of opinion that the solid protoxide of nitrogen may be employed with still greater advantage than solid carbonic acid for producing intense cold by its evaporation in vacuo, when mixed with ether. It became solid in vacuo under the intense cold of —148°, at which temperature the tension of its vapour was less than one atmosphere.

BINOXIDE OF NITROGEN.

Hist.—Discovered by Hales, but first carefully studied by Priestley, under the name of *nitrous gas.* It is also called *nitric oxide*, and *deutoxide of nitrogen.*

Prep.—Preferably by the action of nitric acid, of sp. gr. 1·2, on metallic copper. Brisk effervescence takes place without the aid of heat, and the gas may be collected over water or mercury. The copper gradually disappears during the process; the liquid acquires a beautiful blue colour, and yields on evaporation a salt which is composed of nitric acid and oxide of copper. The chemical changes that occur are the following:—One portion of nitric acid suffers decomposition: part of its oxygen oxidizes the copper; while another part is retained by the nitrogen of the nitric acid, forming binoxide of nitrogen. The oxide of copper attaches itself to some undecomposed nitric acid, and forms the blue nitrate. Many other metals are oxidized by nitric acid, with disengagement of a similar compound; but none, mercury excepted, yields so pure a gas as copper. The following equation expresses the reaction:—

$$Cu_3 + 4NO_5 = 3(CuO,NO_5) + NO_2.$$

Prop.—Gaseous, not hitherto condensed into a liquid; colourless, tasteless, and inodorous; excites violent spasm of the glottis when an attempt is made to inhale it; sp. gr. = 1·0377, and 100 C. I. weigh 32·137 grains. Water at 60° dissolves about 11 per cent. It has no action on test paper; but if any free oxygen is present, it produces dense, suffocating, acid vapours of a red or orange colour, called *nitrous acid vapours*, which are freely absorbed by water, and render it acid. This character distinguishes it from all other gases, and is a good test of the presence of free oxygen. In some cases it supports combustion: burning sulphur and a lighted candle are extinguished by it; but charcoal and phosphorus, when in vivid combustion, burn in it with increased brilliancy. The product of the combustion is carbonic acid in the former case, and metaphosphoric acid in the latter, nitrogen being separated in both instances. With an equal bulk of hydrogen it forms a mixture which cannot be made to explode, but which is kindled by contact with a lighted candle, and burns rapidly with a greenish white flame, water and pure nitrogen gas being the sole products. The action of freshly ignited spongy platinum on a mixture of hydrogen and binoxide of nitrogen gases leads to the slow production of water and ammonia.

It is partially resolved into its elements by being passed through red-hot tubes, and a succession of electric sparks has a similar effect. It is converted into protoxide of nitrogen by substances which have a strong affinity for oxygen, such as moist iron filings, and a solution of sulphuret of potassium. Davy ascertained its composition by the combustion of charcoal (Elements of Chemical Philosophy, p. 200). Two volumes of the binoxide yielded one volume of nitrogen, and about one of carbonic acid; whence it was inferred to consist of equal measures of oxygen and nitrogen gases united without any condensation. Gay-Lussac (Mémoires d'Arcueil) proved that this proportion is rigidly exact. He decomposed 100 measures of the gas, by heating potassium in it; when 50 measures of pure nitrogen were left, and the potassa formed corresponded to 50 measures of oxygen. The same fact has been lately proved by Henry (An. of Phil., N. S., viii. 299). Hence, as

50 cubic inches of oxygen gas weigh . . .	17·054 grains
50 do. nitrogen	15·083
100 cubic inches of the binoxide must weigh . .	32·137

From the invariable formation of red-coloured acid vapours, whenever binoxide of nitrogen and oxygen are mixed together, these gases detect the presence of each other with great certainty; and since the product is wholly absorbed by water, either of them may be entirely removed from any gaseous mixture by adding a sufficient quantity of the other. Priestley, who first observed this fact, supposed that combination takes place between them in one proportion only; and inferring on this supposition, that a given absorption must always indicate the same quantity of oxygen, he was led to employ binoxide of nitrogen in Eudiometry. But in this opinion he was mistaken. The discordant results obtained by his method soon excited suspicion of their accuracy; and the source of error has since been discovered by the researches of Dalton and Gay-Lussac. It appears from the experiments of Gay-Lussac, and his results do not differ materially from those of Dalton, that for 100 measures of oxygen, 400 of the binoxide may be absorbed as a maximum, and 133 as a minimum; and that between these extremes, the quantity of the binoxide corresponding to 100 of oxygen is exceedingly variable. It does not follow from this, that oxygen and binoxide of nitrogen unite in every proportion within these limits. The true explanation is, that the mixture of these gases may give rise to three compounds,—hyponitrous, nitrous, and nitric acids; and that either may be formed almost, if not entirely, to the exclusion of the others, if certain precautions are adopted. But in the usual mode of operating, two if not all are generated at the same time, and in a proportion to each other which is by no means uniform. The circumstances that influence the degree of absorption, when a mixture of oxygen and binoxide of nitrogen is made over water, are the following:—1. The diameter of the tube; 2. The rapidity with which the mixture is made; 3. The relative proportion of the two gases; 4. The time allowed to elapse after mixing them; 5. Agitation of the tube; and, lastly, the opposite conditions of adding the oxygen to the binoxide, or the binoxide to the oxygen.

The binoxide may, notwithstanding, be usefully employed in Eudiometry. Dalton operates (An. of Phil. x. 38, and Henry's Elements) by mixing the gases in a graduated tube about half an inch wide over water, and waiting, without agitating the mixture, till decrease of volume is at an end, which usually occurs in less than 6 or 10 minutes. Every 27 measures which have disappeared, indicate 10 of oxygen. A large excess of the binoxide should be avoided; and if the gas under examination contain more than 20 per cent. of oxygen, it should be previously diluted with nitrogen. Gay-Lussac advises that 100 measures of the gas under examination should be introduced into a very wide tube or jar, and that an equal volume of the binoxide should then be added (Mém. d'Arcueil, ii. 247). The red vapours, which are instantly produced, disappear very quickly; and the absorption, after half a minute, or a minute at the most, may be regarded as complete. The residue is then transferred into a graduated tube and measured. One-fourth of the loss is oxygen.—Results very near the truth may be obtained by both methods.

If a current of the binoxide be conducted into a solution of protosulphate of iron, the gas is absorbed in large quantity, and the solution acquires a deep olive-brown colour, which appears almost black when fully saturated. This solution absorbs oxygen with facility. But it cannot be safely employed in Eudiometry; because the absorption of oxygen is accompanied, or at least very soon followed, by evolution of gas from the liquid itself. The binoxide is combined with the sulphate in the ratio of 1 eq. of the former to 4 eq. of the latter; and the gas may be recovered by exposure to a vacuum, the original salt being left unchanged (Péligot, in An. de Ch. et Ph. liv. 17). On applying heat, part of the gas is evolved and part decomposed: the protoxide of iron takes oxygen both from the binoxide and from water, forming peroxide of iron; while the hydrogen of the decomposed water and nitrogen of the binoxide combine together, and generate ammonia. Nitric acid is formed when the solution is exposed to the air or oxygen gas, but not otherwise (Davy). When a mixture of binoxide of nitrogen and sulphurous acid are brought into contact with a solution of potassa or ammonia, both gases are absorbed, and a peculiar acid is generated, which has been called by Pelouze, its discoverer, *nitrosulphuric acid.* It is composed of 1 eq. of nitrogen, 1 of sulphur, and 4 of oxygen, 200 volumes of binoxide of nitrogen combining with 100 of sulphurous acid. The nitrosulphates are very prone to decomposition, a sulphate being formed with the evolution of protoxide of nitrogen: this ensues by the mere contact of certain substances, which do not themselves undergo any change, such as spongy platinum, silver and its oxide, charcoal powder, peroxide of manganese, and solutions of corrosive sublimate, lunar caustic, and the sulphates of the oxides of zinc, copper, and iron. The same effect is produced by an acid, as when an attempt is made to procure nitrosulphuric acid in a separate state, even the carbonic acid of the atmosphere being capable of causing the decomposition. The crystals of the nitrosulphates of potash and ammonia may be preserved in well-stopped bottles at ordinary temperatures; the solutions, on the contrary, are not stable above the freezing point, but the stability is much increased by an excess of alkali. On this is founded the best mode of preparing the nitrosulphates, which consists in transmitting binoxide of nitrogen through a strong solution of sulphite of ammonia or potash with an excess of alkali, when the corresponding nitrosulphate separates in colourless prismatic or acicular crystals. The dry crystals decompose at a moderate heat, namely, at 230° for the ammoniacal salt, and 266° for that of potash, the former giving rise to a slight explosion owing to the rapid evolution of protoxide of nitrogen. The decomposition of the nitrosulphate of potassa by heat is particularly interesting, from its forming sulphite of potassa and binoxide of nitrogen instead of sulphate of potassa and the protoxide, as occurs in every other instance. (Lieb. Ann. xv. 240.)

It is singular that both binoxide and protoxide of nitrogen, notwithstanding the absence of acidity, are capable of forming compounds of considerable permanence with the pure alkalies.

Its eq. is $= 30{\cdot}15$; eq. vol. $= 200$; symb. $N + 2O$, NO_2, or $\ddot{N}$.

HYPONITROUS ACID.

Hist. and Prep—First prepared by Gay-Lussac, who shewed that on adding binoxide of nitrogen in excess to oxygen gas, confined in a glass tube over mercury, the absorption is always uniform, provided a strong solution of pure potassa is put into the tube before mixing the two gases: 50 measures of oxygen gas combine under these circumstances with 200 of the binoxide, forming an acid which unites with the potassa. As the binoxide contains half its volume of oxygen gas, the new acid must be composed of 100 measures of nitrogen and 150 of oxygen, as already stated. It is generated when the binoxide is kept for a considerable time, say three months, in a glass tube over mercury, with a strong solution of pure potassa, when the binoxide is resolved into hyponitrous acid, which unites with the alkali, while protoxide of nitrogen remains in the tube; and Dulong formed it by mixing 200 measures of binoxide of nitrogen with 50 of oxygen gas, both quite dry, and exposing the resulting orange fumes to intense cold, which condensed it into a liquid. It is the *nitrous* acid of Berzelius and other Continental chemists.

Prop.—At 0° it is a colourless liquid, and green at common temperatures. It is so volatile, that in open vessels the green fluid wholly and rapidly passes off in the form of an orange vapour, which is said by Mitscherlich to have a density of 1·72. On admixture with water it is converted into nitric acid and binoxide of nitrogen, the latter escaping with effervescence; but when much nitric acid is present, the hyponitrous is changed into nitrous acid, the presence of which imparts several shades of colour, orange, yellow, green, and blue, according as its quantity is more or less predominant. One eq. of hyponitrous and one of nitric acid yield 2 eq. of nitrous acid. Thus NO_3 and NO_5 obviously contain the elements for forming $2NO_4$.

Hyponitrous acid does not unite directly with alkalies, being then resolved principally into nitric acid and binoxide of nitrogen; but the hyponitrites of the alkalies and alkaline earths may be obtained by heating the corresponding nitrates to a gentle red-heat; and the hyponitrite of the oxide of lead is formed by boiling a solution of the nitrate of that oxide with metallic lead.

Hyponitrous acid forms with water and sulphuric acid a crystalline compound, which is formed in large quantity during the manufacture of sulphuric acid, and the production of which is an essential part of that process. It is generated whenever moist sulphurous acid gas and nitrous acid vapour are intermixed, being instantly deposited in the form of white acicular crystals: and Gay-Lussac discovered that it may also be made by the direct action of anhydrous nitrous and strong sulphuric acid. The first attempt to determine its composition analytically was by Henry, who found it to consist of 1 eq. of hyponitrous acid, 5 of sulphuric acid, and 5 of water. (Ann. of Phil. xxvii. 367.) G. de Claubry has lately repeated the analysis of the same compound in a state of more perfect dryness, and by what he considers a better method; and he gives as its constituents 2 eq. of hyponitrous acid, 4 of water, and 5 of sulphuric acid. (An. de Ch. et Ph. xlv. 284.) The theory of its production has been very carefully studied by De Claubry. It appears that when moist sulphurous and nitrous acids react on each other, the former is converted into sulphuric and the latter into hyponitrous acid, the oxygen lost by one being gained by the other, $NO_4 + SO_2 = NO_3 + SO_3$. A little nitrogen gas is always disengaged at the same time, which can only arise from a small portion of nitrous acid losing the whole of its oxygen. The action of sulphuric on nitrous acid is different: in this case the nitrous acid is resolved into nitric and hyponitrous acids, $2NO_4 = NO_5 + NO_3$, the latter uniting with sulphuric acid and most of its water to produce the crystalline solid, while the remainder of the water unites with the nitric acid. When the crystalline matter is put into water, the hyponitrous is resolved into nitrous acid and binoxide of nitrogen, both of which escape with effervescence, $2NO_3 = NO_4 + NO_2$. If much water is present, more or less of the nitrous acid is converted into nitric acid and the binoxide. Similar changes ensue when the crystals are exposed to the air, humidity being rapidly absorbed. This subject has also been examined by Bussy with similar results.

Its eq. is $= 38{\cdot}15$; symb. $N + 3O$, NO_3, or $\dddot{N}$.

NITROUS ACID.

Prep.—It is always formed when binoxide of nitrogen and oxygen gases are intermixed. Davy shewed, by making the mixture in a dry glass vessel previously exhausted, that nitrous acid vapour is formed by the action of 200 measures of the binoxide on 100 of oxygen gas; and hence, as 200 of the binoxide contains 100 of nitrogen and 100 of oxygen, nitrous acid was inferred to consist of 100 measures of nitrogen united with 200 of oxygen gas (page 205). This inference has been confirmed by the researches of Gay-Lussac and Dulong (An. de Ch. et Ph. i. and ii.), the former of whom also proved that its elements contract to 1-3rd of their volume, or, in other words, 100 measures of nitrous acid vapour contain 100 of nitrogen gas and 200 of oxygen. The specific gravity of this vapour ought to be 3·1777, formed of 0·9727 the sp. gr. of nitrogen + 2·2050 twice the sp. gr. of oxygen. It is best prepared by heating to redness in an earthen retort the nitrate of oxide of lead, carefully dried; when the nitric acid is resolved into nitrous acid and oxygen, and on receiving the products in a dry tube, surrounded by a mixture of ice and salt, the former is condensed. The following equation represents the decomposition:—

$$PbO,NO_5 = PbO + O + NO_4.$$

Prop.—An anhydrous liquid of sp. gr. 1·451, and orange colour at 60°, yellow at 32°, and almost colourless at 0°; acid, pungent, and powerfully corrosive; and imparts a yellow stain to the skin. It is very volatile, boiling at 82°: in a stopped bottle it preserves its liquid form at 60°; but when exposed to the atmosphere it is rapidly dissipated in orange-red fumes, which when once mixed with air or other gases require intense cold for condensation.

Nitrous acid vapour is characterized by its orange-red colour, acid reaction, and by being absorbed by water with disengagement of binoxide of nitrogen and formation of nitric acid. It is quite irrespirable, exciting great irritation and spasm of the glottis, even when moderately diluted with air. A taper burns in it with considerable brilliancy. It extinguishes burning sulphur; but the combustion of phosphorus continues in it with great vividness.

Nitrous acid is a powerful oxidizing agent, readily giving oxygen to the more oxidable metals, and to most substances which have a strong affinity for it. The acid is decomposed at the same time, being commonly changed into binoxide of nitrogen, though sometimes the protoxide and even pure nitrogen gases are evolved. When transmitted through a red-hot porcelain tube it suffers decomposition, and a mixture of oxygen and nitrogen gases is obtained.

When nitrous acid is mixed with a considerable quantity of water, it is instantly resolved into nitric acid, which unites with the water, and binoxide of nitrogen which escapes with effervescence. Three eq. of nitrous acid yield 2 eq. of nitric acid and one of the binoxide; for $3NO_4 = 2NO_5 + NO_2$. When a rather small quantity of water is used, the evolved binoxide, at first considerable, becomes less and less as successive quantities of nitrous acid are added, till at last the evolution of gas ceases altogether. The colour of the solution varies remarkably during the process: from being colourless, the liquid acquires a blue tint, then passes into bluish green, green, yellow, and lastly orange. These different solutions contain different relative quantities of nitric acid, nitrous acid, and water, on which circumstance the varying shades of colour depend. Nitric and nitrous acids are disposed to unite with each other, and the influence of this attraction enables nitrous acid to sustain admixture with water without decomposition. Strong nitric acid will unite with a considerable quantity of nitrous acid, and thereby acquires an orange-red tint. In a weaker nitric acid the water decomposes part of the nitrous acid, and the colour of the solution is orange or yellow. As the strength of the nitric acid becomes weaker and weaker, the quantity of nitrous acid which it can protect from decomposition become less and less, and the colour of the solution varies from yellow to green and blue, and is at length colourless. These changes may be witnessed, not only by adding successive quantities of nitrous acid to water, and thereby at length producing a strong nitric acid, but commencing with the latter, saturating it with nitrous acid, and then successively diluting with water.

When nitrous acid is mixed with a very small quantity of water, no binoxide of nitrogen is disengaged, but the liquid becomes green, like the colour of hyponitrous acid. I have repeatedly obtained a similar liquid in preparing nitrous acid from nitrate of oxide of lead, when the materials were not adequately dried; and that green liquid, when allowed to dissipate in the air, leaves some nitric acid behind. From these facts it seems probable that in the decomposition of nitrous acid by water, the first change is the conversion of nitrous into nitric and hyponitrous acids, which last is subsequently changed, when the required quantity of water is present, into nitric acid and binoxide of nitrogen. It may thus well happen that hyponitrous acid contributes to produce the varying colours above described.

Some chemists consider nitrous acid as a compound of nitric and hyponitrous acids, rather than of nitrogen and oxygen. In fact, on adding nitrous acid to an alkaline solution, we obtain a nitrate and hyponitrite; a circumstance which has given rise to the notion that nitrous acid cannot act as a distinct acid.

Its eq. is 46·15; eq. vol. $= 100$; symb. $N + 4O$, NO_4, or $\overset{....}{N}$.

NITRIC ACID.

Hist.—If a succession of electric sparks be passed through a mixture of oxygen and nitrogen gases confined in a glass tube over mercury, a little water being present, the volume of gases will gradually diminish, and the water after a time will be found to have acquired acid properties. On neutralizing the solution with potassa, or, what is better, by putting a solution of that alkali instead of water into the tube at the beginning of the experiment, a salt is obtained which possesses all the properties of nitrate of potassa. This experiment was performed in

1785 by Cavendish, who inferred from it that nitric acid is composed of oxygen and nitrogen, though the acid itself, under the name of *spirit of nitre*, had been long previously known. The best proportion of the gases was found to be seven of oxygen to three of nitrogen; but as some nitrous acid is always formed during the process, the exact composition of nitric acid cannot in this way be accurately determined.

Nitric acid may be formed much more conveniently by adding binoxide of nitrogen slowly over water to an excess of oxygen gas. Gay-Lussac proved that nitric acid may in this manner be obtained quite free from nitrous or hyponitrous acid; and that it is composed of 100 measures of nitrogen and 250 of oxygen, a result fully confirmed by Davy, Henry, Berzelius, and others.

Nitric acid cannot exist in an insulated state. Binoxide of nitrogen and oxygen gases never form nitric acid if mixed together when quite dry; and nitrous acid vapour may be kept in contact with oxygen gas without change, provided no water is present. The most simple form under which chemists have hitherto procured nitric acid is in solution with water; a liquid which, in its concentrated state, is the nitric acid of the pharmacopœia. By manufacturers it is better known by the name of *aqua fortis.*

The nitric acid of commerce is procured by decomposing some salt of nitric acid by means of oil of vitriol, and common nitre, as the cheapest of the nitrates, is employed for the purpose. This salt, previously well dried, is put into a glass retort, and a quantity of the strongest oil of vitriol is poured upon it. On applying heat, ebullition ensues, owing to the escape of nitric acid vapours, which must be collected in a receiver kept cold by moist cloths. The heat should be steadily increased during the operation, and continued as long as any acid vapours come over.

Chemists differ as to the best proportions for forming nitric acid. The London College recommends equal weights of nitre and oil of vitriol; and the Edinburgh and Dublin Colleges employ three parts of nitre to two of the acid. In the process of the London College the alkali of the nitre is left as a bisulphate in the retort; since one eq. of nitre (54 nitric acid and 47 potassa) is 100, and the nearly equal number 98 corresponds to 2 eq. of oil of vitriol, which contain 2 eq. of anhydrous sulphuric acid and 2 eq. of water. During the distillation the nitric acid passes over along with 1 eq. of water, and 1. eq. of water is retained by the bisulphate of potassa. The reaction may be thus expressed:—

$$\mathrm{KO,NO_5} + 2\,(\mathrm{HO,SO_3}) = \mathrm{HO,NO_5} + (\mathrm{KO,HO,2SO_3}).$$

The presence of water is essential; nitric acid of 1·50 consists of real or anhydrous acid and water in the ratio of 1 eq. of each, and unless water in at least this proportion be supplied, a proportional quantity of nitric acid is resolved, at the moment of quitting the potassa, into oxygen and nitrous acid (Phillips, in Phil. Mag. ii. 430). If the mixture be introduced into the retort without soiling its neck, and the heat be cautiously raised, the product will be quite free from sulphuric acid; and therefore the second distillation from nitre, recommended in the pharmacopœia, is superfluous. Even where the neck of the retort has been soiled, the second distillation is unnecessary, for we have only to collect separately the first portions of the distilled acid, by which the neck of the retort is washed. The receiver being changed as soon as the acid dropping from the retort is found to be pure, the subsequent portions will be found absolutely pure. It is seldom necessary to reject more than the first tenth of the acid, and that, although impure, may be used for many purposes.

The proportions of the Edinburgh and Dublin Colleges are such, that the residual salt is a mixture of sulphate and bisulphate of potassa. The acid of the nitre does not receive from the oil of vitriol the requisite quantity of water, and hence part of it is decomposed, yielding towards the close of the operation an abundant supply of nitrous acid fumes. If the receiver be kept cool, nearly all these vapours are condensed, and the product is a mixture of nitric and nitrous acids, of a deep orange-red colour, very strong and fuming, and of a greater sp. gr., though proportionally less in quantity, than that obtained by the foregoing process. The sp. gr. of the pale acid is 1·500; while that of the red acid is 1·520, or by previously drying the nitre and boiling the sulphuric acid, Hope states that it may be made so high as 1·54.

Some manufacturers decompose nitre with half its weight of sulphuric acid, thus employing the ingredients in the proportion of 1 eq. of each. In this case about half of the nitric acid is decomposed, and considerable loss sustained, unless the requisite quantity of water is previously mixed with the sulphuric acid, or water be placed in the receiver to condense the nitrous acid. Some of the nitre is likewise apt to escape decomposition; and the residue, consisting of neutral sulphate, which is much less soluble than the bisulphate, is removed from the retort with difficulty.

In none of the preceding processes, not even in the first, is the product quite colourless; for at the commencement and close of the operation, nitrous acid fumes are disengaged, which communicate a straw-yellow or an orange-red tint, according to their quantity. If a very pale acid is required, two receivers should be used; one for condensing the colourless vapours of nitric acid, and another for the coloured products. The coloured acid is called nitrous acid by the College; but it is in reality a mixture or compound of nitric and nitrous acids, similar to what may be obtained by mixing anhydrous nitrous with colourless nitric acid. It is easy to convert the common mixed acid of the College into colourless nitric acid, by exposing the former to a gentle heat for some time, when all the nitrous acid will be expelled. But this process is rarely necessary, as the coloured acid may be substituted in most cases for that which is colourless. Where an acid of great strength is required, the former is even preferable.

Nitric acid frequently contains portions of sulphuric and hydrochloric acid. The former is derived from the acid which is used in the process, and the latter from sea-salt, which is frequently mixed with nitre. These impurities may be detected by adding a few drops of a solution of chloride of barium and nitrate of oxide of silver to separate portions of nitric acid, diluted with three or four parts of distilled water. If chloride of barium cause a cloudiness or precipitate, sulphuric acid must be present; if a similar effect be produced by nitrate of oxide of silver, the presence of hydrochloric acid may be inferred. Nitric acid is purified from sulphuric acid by redistilling it from a small quantity of nitrate of potassa, with the alkali of which the sulphuric acid unites, and remains in the retort. To separate hydrochloric acid, it is necessary to drop a solution of nitrate of oxide of silver into the nitric acid as long as a precipitate is formed, and draw off the pure acid by distillation.

Prop.—A strong, highly corrosive acid; in its purest and most concentrated state a colourless liquid, of sp. gr. 1·50 or 1·510, chemically combined with water, from which it cannot be separated without decomposition, or by uniting with some other body. An acid of sp. gr. 1·50 contains 25 per cent. of water, according to the experiments of Phillips, and 20·3 per cent. according to those of Ure.* Nitric acid of this strength emits dense, white, suffocating vapours when exposed to the atmosphere. It attracts watery vapour from the air, whereby its density is diminished. A rise of temperature is occasioned by mixing it with a certain quantity of water. When 58 measures of nitric acid of sp. gr. 1·5 are suddenly mixed with 42 of water, the temperature rises from 60° to 140°; and the mixture, on cooling to 60°, occupies the space of 92·65 measures instead of 100. From its strong affinity for water, it occasions snow to liquefy with great rapidity; and if the mixture is made in due proportion, intense cold will be generated. It boils at 248°, and may be distilled without suffering material change. An acid of lower density than 1·42 becomes stronger by being heated; because the water evaporates more rapidly than the acid. An acid, on the contrary, which is stronger than 1·42 is weakened by the application of heat. It may be frozen by cold: the point of congelation varies with the strength of the acid. The strongest acid freezes at about 50° below zero. When diluted with half its weight of water, it becomes solid at $-1\frac{1}{2}°$; but a little more water lowers its freezing point to $-45°$. It acts powerfully on oxidable substances, and is hence much employed by chemists for bringing bodies to their maximum of oxidation. Nearly all the metals are oxidized by it; and some of them, such as tin, copper, and mercury, are attacked with great violence. If flung on burning charcoal, it increases the brilliancy of its combustion in a high degree. Sulphur and phosphorus are converted into acids by its action. All vegetable substances are decomposed by it. In general the oxygen of the nitric acid enters into direct combination with the hydrogen and carbon of those compounds, forming water with the former, and carbonic acid with the latter. This happens remarkably in those compounds in which hydrogen and carbon are predominant, as in alcohol and the oils. It effects the decomposition of animal matters also. The cuticle and nails receive a permanent yellow stain when touched with it; and if applied to the skin in sufficient quantity it acts as a powerful cautery, destroying the organization of the part entirely.

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* See his Table in the Appendix, showing the strength of diluted acid of different densities.

When oxidation is effected through the medium of nitric acid, the acid itself is commonly converted into binoxide of nitrogen. This gas is sometimes given off nearly quite pure; but in general some nitrous acid, protoxide of nitrogen, or pure nitrogen, is evolved at the same time. The escape of nitrous acid in these cases seems owing, according to some late observations of Phillips, not so much to its direct formation, as to the binoxide at first formed acting on the nitric acid of the solution. Direct solar light deoxidizes nitric acid, resolving a portion of it into oxygen and nitrous acid. The former escapes as gas; the latter is absorbed by the nitric acid, and converts it into the mixed nitrous acid of the shops. When the vapour of nitric acid is transmitted through red-hot porcelain tubes, it suffers complete decomposition, and a mixture of oxygen and nitrogen gases is the product.

Nitric acid may also be deoxidized by transmitting a current of binoxide of nitrogen through it. That gas, by taking oxygen from the nitric, is converted into nitrous acid; and a portion of nitric acid, by losing oxygen, passes into the same compound. The nitrous acid, thus derived from two sources, gives a colour to the nitric acid, the depth and kind of which depend on the strength of the acid. On saturating with binoxide of nitrogen four separate portions of nitric acid of sp. gr. 1·15, 1·35, 1·40, and 1·50, the colour will be blue in the first, green in the second, yellow in the third, and brownish red in the fourth; and acid of 1·05 is not coloured at all. Phillips found that acid of density 1·497 acquired a density 1·541, that is, was made stronger by saturation with the binoxide; but those acids which become green are much weakened, because nitrous acid vapour is mechanically carried off by those portions of binoxide which pass unabsorbed through the liquid.

Tests.—All the salts of nitric acid are soluble in water, and therefore it is impossible to precipitate that acid by any reagent. The presence of nitric acid, when uncombined, is readily detected by its strong action on copper and mercury, emitting ruddy fumes of nitrous acid, and by its forming with potassa a neutral salt, which crystallizes in prisms, and has all the properties of nitre. Gold leaf is a still more delicate test. When hydrochloric acid is added to the solution of a nitrate, chlorine is disengaged, and the liquid hence acquires the property of dissolving gold leaf; but as the action of hydrochloric acid on the salts of chloric, bromic, iodic, and selenic acids likewise yields a solution capable of dissolving gold, no inference can be drawn from the experiment, unless the absence of these acids shall have been previously demonstrated. Another character which may be useful is to mix the supposed nitric acid or nitrate with dilute sulphuric acid in a tube, add a few fragments of pure zinc, and set fire to the hydrogen as it issues; if nitric acid be present, the flame of the hydrogen will have a greenish white tint, due to admixture with binoxide of nitrogen. This test occurred to my assistant, Mr. Balmain; and Mr. Maitland at the same time proposed alcohol instead of zinc with the same intention. A very delicate test has been proposed by O'Shaugnessy, founded on the orange red followed by a yellow colour, which nitric acid communicates to morphia. The supposed nitrate is heated in a test tube with a drop of sulphuric acid, and then a crystal of morphia is added. (Lancet, 1829-30.) It is advisable to try the process in a separate tube with the sulphuric acid alone, in order to prove the absence of nitric acid in it. But the most delicate test is the following, proposed by Derbanius de Richement:—The suspected substance is mixed with pure sulphuric acid in a tube, and gently warmed, and a solution of green vitriol cautiously added. At the line of junction of the two liquids, the dark colour produced by the action of nitric acid on the protosulphate of iron is distinctly seen, even when only $\frac{1}{24000}$ of nitric acid is present.

SECTION VI.

CARBON.

Hist and Prep.—It occurs pure and crystallized in forms of the octohedral system in the diamond, a mineral of unknown origin, but probably derived from the slow decomposition of vegetable matter. It is sometimes a constituent of rocks in the form of small tabular crystals called graphite, and in larger masses mixed with iron, as plumbago with which pencils are made, and in anthracite mixed with earth and metallic sulphurets. It is the essential principle of the different varieties of charcoal—the black mass left when most vegetable and animal matters are heated to redness in close vessels, and which contains any fixed principles originally present in its source. Common charcoal is made from wood, and contains about 1-50th of its weight of alkaline and earthy salts, which constitute the ashes when wood-charcoal is burned. Coke is the charcoal from coal, ivory black or animal charcoal is that from bones, lamp-black from resin. Very pure varieties of charcoal may be formed from spirit of wine, turpentine, sugar, and starch.

Prop.—Carbon, as it exists in the diamond, is the hardest substance in nature; sp. gr. 3·52; it crystallizes in the regular system in forms which are frequently hemihedral, and are characterized by a perfect cleavage parallel to the faces of the octohedron; beautifully transparent and a powerful refractor of light; a non-conductor of heat and electricity. It is very unchangeable, resists the action of acids and alkalies, and bears the most intense heat in close vessels without fusing or undergoing any perceptible change. Heated to redness in the open air, it is entirely consumed. Newton first suspected it to be combustible from its great refracting power, a conjecture which was rendered probable by the experiments of the Florentine academicians in 1694. Lavoisier first proved it to contain carbon by throwing the sun's rays, concentrated by a powerful lens, upon a diamond contained in a vessel of oxygen gas. The diamond was consumed entirely, oxygen disappeared, and carbonic acid was generated. It has since been demonstrated by the researches of Guyton-Morveau, Smithson Tennant, Allen and Pepys, and Davy, that carbonic acid is the product of its combustion. Guyton-Morveau inferred from his experiments that the diamond is pure carbon, and that charcoal is an oxide of carbon. Tennant burned diamonds by heating them with nitre in a gold tube; and comparing his own results with those of Lavoisier on the combustion of charcoal, he concluded that equal weights of diamond and pure charcoal, in combining with oxygen, yield precisely equal quantities of carbonic acid. He was thus induced to adopt the opinion, that charcoal and the diamond are chemically the same substance; and that the difference of their physical character is solely dependent on a difference of aggregation.* This conclusion was confirmed by the experiments of Allen and Pepys †, and Davy ‡, who compared the product of the combustion of the diamond with that derived from different kinds of charcoal. The latter chemist did indeed observe the production of a minute quantity of water during the combustion of the purest charcoal, indicative of a trace of hydrogen ; but its quantity is so small, that it cannot be regarded as a necessary constituent. It proves only that a trace of hydrogen is retained by charcoal with such force, that it cannot be expelled by the temperature of ignition.

Charcoal, as obtained from wood, is hard and brittle, conducts heat very slowly, but is a good conductor of electricity; quite insoluble in water, is attacked with difficulty by nitric acid, and is little affected by any of the other acids, or by the alkalies. It undergoes little change from exposure to air and moisture, being less injured under these circumstances than wood. It is exceedingly refractory in the fire, if excluded from the air, supporting the most intense heat which chemists are able to produce without change.

It possesses the property of absorbing a large quantity of air or other gases at common temperatures, and of yielding the greater part of them again when it is heated. It appears from the researches of Saussure, that different gases are absorbed by it in different proportions. His experiments were performed by plunging a piece of red-hot charcoal under mercury, and introducing it when cool into the gas to be absorbed. He found that charcoal prepared from box-wood absorbs, during the space of 24 or 36 hours, of

Ammoniacal Gas	90 times its volume.
Muriatic Acid	85
Sulphurous Acid	65
Sulphuretted Hydrogen	81 (Dr. C. Henry.)
Nitrous Oxide	40
Carbonic Acid	35
Olefiant Gas	35
Carbonic Oxide	9·42
Oxygen	9·25
Nitrogen	7·5
Hydrogen	1·75

The absorbing power of charcoal, with respect to gases, cannot be attributed to chemical action ; for the quantity of each gas which is absorbed bears no relation whatever to its affinity for charcoal. The effect is in reality owing to the peculiar porous texture of that substance, which enables it, in common with most spongy bodies, to absorb more or less of all gases, vapours, and liquids with which it is in contact. This property is most remarkable in charcoal prepared from wood, especially in the compact varieties of it, the pores of which are numerous and small. It is materially diminished by reducing the charcoal to powder; and in plumbago, which has not the requisite degree of porosity, it is wanting altogether.

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* Phil. Trans. 1797. † Ibid. 1807. ‡ Ibid. 1814.

The porous texture of charcoal accounts for the general fact of absorption only; its power of absorbing more of one gas than of another, must be explained on a different principle. This effect, though modified to all appearance by the influence of chemical attraction, seems to depend chiefly on the natural elasticity of the gases. Those which possess such a great degree of elasticity as to have hitherto resisted all attempts to condense them into liquids, are absorbed in the smallest proportion; while those that admit of being converted into liquids by compression, are absorbed more freely. For this reason, charcoal absorbs vapours more easily than gases, and liquids than either.

Allen and Pepys determined experimentally the increase in weight experienced by different kinds of charcoal, recently ignited, after a week's exposure to the atmosphere. The charcoal from fir gained 13 per cent.; that from *lignum vitæ*, 9·6; that from box, 14; from beech, 16·3; from oak, 16·5; and from mahogany, 18. The absorption is most rapid during the first 24 hours. The substance absorbed is both water and atmospheric air, which the charcoal retains with such force that it cannot be completely separated from them without exposure to a red heat. Vogel has observed that charcoal absorbs oxygen in a much greater proportion from the air than nitrogen. Thus, when recently ignited charcoal, cooled under mercury, was put into a jar of atmospheric air, the residue contained only 8 per cent. of oxygen gas; and if red-hot charcoal be plunged into water, and then introduced into a vessel of air, the oxygen disappears almost entirely. It is said that pure nitrogen may be obtained in this way. (Schweigger's Journal, iv.)

Charcoal likewise absorbs the odoriferous and colouring principles of most animal and vegetable substances. When coloured infusions of this kind are digested with a due quantity of charcoal, a solution is obtained, which is nearly if not quite colourless. Tainted flesh may be deprived of its odour by this means, and foul water be purified by filtration through charcoal. The substance commonly employed to decolorize fluids is animal charcoal reduced to a fine powder. It loses the property of absorbing colouring matters by use, but recovers it by being heated to redness.

Charcoal is highly combustible. When strongly heated in the open air, it takes fire, and burns slowly. In oxygen gas, its combustion is lively, and accompanied with the emission of sparks. In both cases it is consumed without flame, smoke, or residue, if quite pure; and carbonic acid gas is the product of its combustion.

Its eq. is = 6·12; its vapour (theoretical, p. 162) has a sp. gr. = 0·4215, and eq. vol. = 100, and 100 C. I. weigh 13·153 grains.

The composition of the compounds of carbon described in this section is as follows:—

	Carbon.		Oxygen.		Equiv.	Formulæ.
Carbonic Oxide	6·12 or 1 eq.	+	8 or 1 eq.	=	14·12	$C+O$ or CO.
Carbonic Acid	6·12 or 1 eq.	+	16 or 2 eq.	=	22·12	$C+2O$ or CO_2.

Carbonic oxide gas is theoretically considered as a compound of 100 measures of the vapour of carbon and 50 of oxygen condensed into 100 measures; and carbonic acid gas, of 100 measures of the vapour of carbon and 100 of oxygen condensed into 100 measures.

CARBONIC ACID.

Hist.—Discovered by Black in 1757, and described by him in his inaugural dissertation on magnesia under the name of *fixed air*. He observed the existence of this gas in common limestone and magnesia, and found that it may be expelled from these substances by the action of heat or acids. He also remarked that the same gas is formed during respiration, fermentation, and combustion. Its composition was first demonstrated synthetically by Lavoisier, who burned carbon in oxygen gas, and obtained carbonic acid as the product. The same experiment has been repeated by Davy, Allen, and Pepys, and others, with the result that in the combustion of diamond or other pure carbonaceous matter the oxygen undergoes no change of volume, or, in other words, that carbonic acid gas contains its own volume of oxygen: hence the difference of the sp. gravities of carbonic acid and oxygen gases (1·524 – 1·1025), or 0·4215, gives the exact ratio of the quantities of carbon and oxygen combined, being 0·4215 to 1·1025, or 6·12 to 16. Smithson Tennant illustrated its nature analytically by passing the vapour of phosphorus over chalk, or carbonate of lime, heated to redness in a glass tube. The phosphorus took oxygen from the carbonic acid, charcoal in the form of a light black powder was deposited, and the phosphoric acid, which was formed, united with the lime.

Prep.—Conveniently by the action of hydrochloric acid, diluted with two or three times its weight of water, on fragments of marble, when carbonic acid gas escapes with effervescence, and chloride of calcium is left in solution.

Prop.—It is a colourless gas of a pungent odour and acidulous taste, condensable at 32° by a pressure of 36 atmospheres into a liquid, which congeals by the cold produced by its own evaporation, estimated at — 180°, and at that temperature is solid under the atmospheric pressure, being the first instance of a solidified gas. The sp. gr. of the gas is 1·524, and 100 C. I. at 60° and 30′ Bar. weigh 47·262 grains; the sp. gr. of the liquid at 32° is 0·83; it dilates remarkably from heat, its expansion being upwards of four times that of air, 20 volumes of the liquid at 32° occupying 29 volumes at 86°, and its sp. gr. varies from 0·9 to 0·6 as the temperature rises from — 4° to + 86°. When heated from 32° to 86° its elasticity rises from 36 to 73 atmospheres, being 0·68 of an atmosphere for each degree. It is insoluble in water and fat oils, but soluble in all proportions in ether, alcohol, naphtha, oil of turpentine, and bisulphuret of carbon. The evaporation of its ethereal solution causes an intense degree of cold, by which large quantities of mercury may be frozen. (Thilorier, in Ann. de Ch. et Ph. lx. 427.)

Carbonic acid gas extinguishes burning substances of all kinds, and the combustion does not cease from the want of oxygen only. It exerts a positive influence in checking combustion, as appears from the fact, that a candle cannot burn in a gaseous mixture composed of four measures of atmospheric air, and one of carbonic acid.

It is not better qualified to support the respiration of animals; for its presence, even in moderate proportion, is soon fatal. An animal cannot live in air which contains sufficient carbonic acid for extinguishing a lighted candle; and hence the practical rule of letting down a burning taper into old wells or pits before any one ventures to descend. If the light is extinguished, the air is certainly impure; and there is generally thought to be no danger, if the candle continues to burn. But some instances have been known of the atmosphere being sufficiently loaded with carbonic acid to produce insensibility, and yet not so impure as to extinguish a burning candle. (Christison on Poisons, 2nd ed., 707.) When an attempt is made to inspire pure carbonic acid, violent spasm of the glottis takes place, which prevents the gas from entering the lungs. If it be so much diluted with air as to admit of its passing the glottis, it then acts as a narcotic poison on the system. It is this gas which has often proved destructive to persons sleeping in a confined room with a pan of burning charcoal.

It is quite incombustible, and cannot be made to unite with an additional portion of oxygen. It is a compound, therefore, in which carbon is in its highest degree of oxidation.

Lime water becomes turbid when brought into contact with carbonic acid. The lime unites with the gas, forming carbonate of lime, which, from its insolubility in water, at first renders the solution milky, and afterwards forms a white flaky precipitate. Hence lime water is not only a valuable test of the presence of carbonic acid, but is frequently used to withdraw it altogether from any gaseous mixture that contains it.

Recently boiled water dissolves its own volume of carbonic acid gas at 60° and 30′ Bar.; but it will take up much more if the pressure be increased. The quantity of the gas absorbed is in exact ratio with the compressing force; that is, water dissolves twice its volume when the pressure is doubled, and three times its volume when the pressure is trebled. A saturated solution may be made by transmitting a stream of the gas through a vessel of cold water during the space of half an hour, or still better by the use of a Woulfe's bottle or Nooth's apparatus, so as to aid the absorption by pressure. Water and other liquids which have been charged with carbonic acid under great pressure, lose the greater part of the gas when the pressure is removed. The effervescence which takes place on opening a bottle of ginger beer, cider, or brisk champaign, is owing to the escape of carbonic acid gas. Water, if fully saturated with carbonic acid gas, sparkles when it is poured from one vessel into another. The solution has an agreeably acidulous taste, and gives to litmus paper a red stain which is lost on exposure to the air. On the addition of lime water to it, a cloudiness is produced, which at first disappears, because the carbonate of lime is soluble in excess of carbonic acid; but a permanent precipitate ensues when the free acid is neutralized by an additional quantity of lime water. The water which contains carbonic acid in solution is wholly deprived of the gas by boiling. Removal of pressure from its surface by means of the air-pump has a similar effect.

The agreeable pungency of beer, porter, and ale is in a great measure owing to the presence of carbonic acid; by the loss of which, on exposure to the air, they become stale. All kinds of spring and well water contain carbonic acid absorbed from the atmosphere, and to its presence they are partly indebted for their pleasant flavour. Boiled water has an insipid taste, from the absence of carbonic acid.

Carbonic acid is always present in the atmosphere, even at the summit of the highest mountains, or at a distance of several thousand feet above the ground. Its presence may be demonstrated by exposing lime water in an open vessel to the air, when its surface will soon be covered with a pellicle, which is carbonate of lime. The origin of the carbonic acid is obvious. Besides being formed abundantly by the combustion of all substances which contain carbon, the respiration of animals is a fruitful source of it, as may be proved by breathing for a few minutes into lime water ; and it is also generated in all the spontaneous changes to which dead animal and vegetable matters are subject. The carbonic acid proceeding from such sources is commonly diffused equably through the air ; but when any of these processes occur in low confined situations, as at the bottom of old wells, the gas is then apt to accumulate there, and form an atmosphere called *choke damp*, which is fatal to any animals that are placed in it. These accumulations happily never take place, except when there is some local origin for the carbonic acid ; as, for example, when it is generated by fermentative processes going on at the surface of the ground, or when it issues directly from the earth, as happens at the Grotto del Cane in Italy, and at Pyrmont in Westphalia. There is no real foundation for the opinion that carbonic acid can separate itself from the great mass of the atmosphere, and accumulate in a low situation merely by the force of gravity. Such a supposition is contrary to the well-known tendency of gases to diffuse themselves equally through each other. It is also contradicted by observation ; for many deep pits, which are free from putrefying organic remains, though otherwise favourably situated for such accumulations, contain pure atmospheric air.

Though carbonic acid is the product of many natural operations, chemists have not hitherto noticed any increase in the quantity contained in the atmosphere. The only known process which tends to prevent increase in its proportion, is that of vegetation. Growing plants purify the air by withdrawing carbonic acid, and yielding an equal volume of pure oxygen in return ; and it is now generally admitted that by this means a full compensation is obtained.

Carbonic acid is contained in the earth. Many mineral springs, such as those of Tunbridge, Pyrmont, and Carlsbad, are highly charged with it. In combination with lime it forms extensive masses of rock, which geologists have found to occur in all countries, and in every formation.

Carbonic acid unites with alkaline substances, and the salts so constituted are called *carbonates*. Its acid properties are feeble, so that it is unable to neutralize completely the alkaline properties of potassa, soda, and lithia. For the same reason, all the carbonates, without exception, are decomposed by the hydrochloric and all the stronger acids; when carbonic acid is displaced, and escapes in the form of gas.

Its eq. is 22·12; eq. vol. = 100; symb. $C + 2O$, CO_2, or $\ddot{C}$.

CARBONIC OXIDE GAS.

Hist.—Priestley discovered it by igniting chalk in a gun-barrel, and afterwards obtained it by heating a mixture of chalk and iron filings. He supposed it to be hydrogen mixed with carbonic acid. Its real nature was pointed out by Cruickshank (Nicholson's Journal, 4to ed., v.), and about the same time by Clément and Désormes. (An. de Chimie, xxxix.)

Prep.—1. By transmitting carbonic acid gas over red-hot fragments of charcoal contained in a tube of iron or porcelain. 2. By igniting alkaline or earthy carbonates with iron filings, charcoal, or some deoxidizing substance. 3. By heating binoxalate of potassa with five or six times its weight of strong oil of vitriol in a retort. Effervescence soon ensues, owing to the escape of gas consisting of equal measures of carbonic acid and carbonic oxide gases; and on absorbing the former by an alkaline solution, the latter is left in a state of perfect purity. To comprehend the theory of the process, it is necessary to premise, that oxalic acid is a compound of equal measures of carbonic acid and carbonic oxide, or at least its elements are in the proportion to form these gases; and that it cannot exist unless in combination with water or some other substance. Now the sulphuric acid unites both with the potassa and water of the binoxalate, and the oxalic acid being thus set free, is instantly decomposed. Oxalic acid may be substituted in this process for binoxalate of potassa. The following equation represents the reaction:—

$$KO,HO,2C_2O_3 + 2SO_8 = KO,HO,2SO_3 + 2CO + 2CO_2.$$

Prop.—A colourless, inodorous gas; sp. gr. = 0·9727, and 100 C. I. at 60° and 30′ Bar. weigh 30·207 grains; has neither acid nor alkaline properties; is sparingly dissolved by water, and does not render lime water turbid. It is inflammable. When a lighted taper is plunged into it, the taper is extinguished; but the gas itself is set on fire, and burns calmly at its surface with a lambent blue flame. The sole product of its combustion, when the gas is quite pure, is carbonic acid; a fact which proves that it does not contain any hydrogen. It cannot support respiration. It acts injuriously on the system; for if diluted with air, and taken into the lungs, it very soon occasions headache and other unpleasant feelings; and when breathed pure, it almost instantly causes profound coma.

A mixture of carbonic oxide and oxygen gases may be made to explode by flame, by a red-hot solid body, or by the electric spark. If mixed together in the ratio of 100 measures of carbonic oxide and rather more than 50 of oxygen, and the mixture is inflamed in Volta's Eudiometer by electricity so as to collect the product of the combustion, the whole of the carbonic oxide, together with 50 measures of oxygen, disappears, and 100 measures of carbonic acid gas occupy their place. From this fact, first ascertained by Berthollet, and since confirmed by subsequent observation, it follows that carbonic oxide contains half as much oxygen, and as much carbon, as carbonic acid. Accordingly its density should be 0·4215 (sp. gr. of carbon vapour) + 0·5512 (half the sp. gr. of oxygen gas) = 0·9727, which is the number found experimentally by Dulong and Berzelius.

The two first processes mentioned for generating carbonic oxide will now be intelligible. The principle of the methods is to bring carbonic acid at a red heat in contact with some substance which has a strong affinity for oxygen. This condition is fulfilled by igniting chalk, or any carbonate which can bear a red heat without decomposition, such as the carbonates of baryta, strontia, soda, potassa, or lithia, with half its weight of iron filings or charcoal. The carbonate is reduced to the caustic state, and its carbonic acid is converted into carbonic oxide by yielding oxygen to the iron or charcoal. When the former is used, oxide of iron is the product; when charcoal is employed, the charcoal itself is oxidized, and yields carbonic oxide. This gas may likewise be generated by heating to redness a mixture of almost any metallic oxide with one-sixth of its weight of charcoal powder. The oxides of zinc, iron, or copper are the cheapest and most convenient. In all these processes it is essential that the ingredients be quite free from moisture and hydrogen, otherwise some carburetted hydrogen gas would be generated. The product should always be washed with lime water, to separate it from carbonic acid.

Henry has ascertained that when a succession of electric sparks is passed through carbonic acid confined over mercury, a portion of that gas is converted into carbonic oxide and oxygen. When a mixture of hydrogen and carbonic acid gases is electrified, a portion of the latter yields one-half of its oxygen to the former; water is generated, and carbonic oxide produced. On electrifying a mixture of equal measures of carbonic oxide and protoxide of nitrogen, both gases are decomposed without change of volume, and the residue consists of equal measures of carbonic acid and nitrogen gases. The carbonic oxide should be in very slight excess, in order to ensure the success of the experiment. On this fact is founded Henry's method of analyzing protoxide of nitrogen, and testing its purity, as will be more particularly mentioned in the fourth part of this work.

Its eq. is 14·12; eq. vol. = 100; symb. C + O, CO, or C.

SECTION VII.

SULPHUR.

Hist.—It occurs as a mineral production in some parts of the earth, particularly in the neighbourhood of volcanoes, as in Italy and Sicily. It is commonly found in a massive state; but it is sometimes met with crystallized in the form of a right rhombic octohedron. It exists much more abundantly in combination with several metals, such as silver, copper, antimony, lead, and iron. It is procured in large quantity by exposing iron pyrites to a red heat in close vessels.

Prop.—A nearly tasteless, brittle solid; colour greenish yellow; odour when rubbed peculiar; sp. gr. 1·99; non-conductor of electricity and heat. Its point of fusion is 232°; between 232° and 280° it possesses the highest degree of fluidity, is then of an amber colour, and if cast into cylindrical moulds, forms the common roll sulphur of commerce. It begins to thicken near 320°, and acquires a reddish tint; and at temperatures between 428° and 482°, it is so tenacious that the vessel may be inverted without causing it to change its place. From 482° to its boiling point it again becomes liquid, but never to the same extent as when at 248°. When heated to at least 428°, and then poured into water, it becomes a ductile mass, which may be used for taking the impression of seals.

Fused sulphur has a tendency to crystallize in cooling. A crystalline arrangement is perceptible in the centre of common roll sulphur; and by good management regular crystals may be obtained. For this purpose several pounds of sulphur should be melted in an earthen crucible; and when partially cooled, the outer solid crust should be pierced, and the crucible quickly inverted, so that the inner and as yet fluid parts may gradually flow out. On breaking the solid mass, when quite cold, crystals of sulphur will be found in its interior.

Sulphur is very volatile. It begins to rise slowly in vapour, even before it is completely fused. At 550° or 600° it volatilizes rapidly, and condenses again unchanged in close vessels. Common sulphur is purified by this process; and if the sublimation be conducted slowly, the sulphur collects in the receiver in the form of detached crystalline grains, called *flowers of sulphur.* In this state, however, it is not quite pure; for the oxygen of the air within the apparatus combines with a portion of sulphur during the process, and forms sulphurous acid. The acid may be removed by washing the flowers repeatedly with water.

The sp. gr. of sulphur vapour was found by Dumas to lie between 6·51 and 6·617, and by Mitscherlich 6·9 (An. de Ch. et Ph. lv. 8): its sp. gr. by calculation (page 163) is 6·648. Hence, could the vapour continue as such at 60° and 30′ Bar., 100 cubic inches should weigh 206·17 grains.

Sulphur is insoluble in water. It dissolves readily in boiling oil of turpentine. The solution has a reddish brown colour like melted sulphur, and if fully saturated deposits numerous small crystals in cooling. It is also soluble in alcohol, if both substances are brought together in the form of vapour. The sulphur is precipitated from the solution by the addition of water.

Sulphur, like charcoal, retains a portion of hydrogen so obstinately that it cannot be wholly freed from it either by fusion or sublimation. Davy detected its presence by exposing sulphur to the strong heat of a powerful galvanic battery, when some hydrosulphuric acid gas was disengaged. The hydrogen, from its minute quantity, can only be regarded in the light of an accidental impurity, and as in nowise essential to the nature of sulphur.

When sulphur is heated in the open air to 300° or a little higher, it kindles spontaneously, and burns with a faint blue light. In oxygen gas its combustion is far more vivid; the flame is much larger, and of a bluish white colour. Sulphurous acid is the product in both instances;—no sulphuric acid is formed even in oxygen gas unless moisture be present.

Crystals of native sulphur, which have been formed by the condensation of sulphurous vapour, as well as those which are deposited from a solution of sulphur in any menstruum, possess forms which are either identical, or connected by being referrible to the same crystalline axes. Such, on the contrary, as are produced by the cooling of fused sulphur in the manner above described, belong to a different system of crystallization. The condition determining the form is temperature: if the crystal be formed below 232°, it belongs to the right prismatic system; if at that point, to the oblique prismatic. This is proved by the influence of temperature on a crystal of either system: a crystal of fusion when first formed is perfectly clear and transparent, but kept at common temperatures, it soon becomes opaque, and presents the appearance of the roll sulphur of commerce: the same change occurs when a native crystal is placed in a solution of a salt which boils at 232°. The opacity is in both cases produced by a new arrangement of the particles of sulphur, by which, without any change in the exterior form, the internal structure of the crystal is altered to correspond to the crystallization peculiar to the temperature.

Berzelius has directed special attention to the fact, that sulphur, although an element, is capable of existing in two or even three forms, which are mechanically distinct, although chemically the same. We have sulphur in the two distinct crystalline forms above mentioned, and to these we may add the plastic form in which it is obtained by being thrown into cold water when at a high temperature. It also occurs in three liquid modifications, when first melted at or a little above its point of fusion; the thick viscid state which occurs when it is further heated, and again the more fluid state which it assumes when heated nearly to its boiling point. Berzelius considers it probable that each of three solid and liquid forms of sulphur has a form of vapour peculiar to itself, the three forms of vapour differing in density and possibly in colour. It is probable that the only form of its vapour we know is that belonging to the liquid form assumed near the boiling point, but we cannot say to which of the solid forms it is to be referred. This form of vapour as we have seen is so dense that its eq. volume is one-sixth of that of hydrogen. There is some reason to believe, from the study of the compounds of sulphur and phosphorus, and from some other circumstances noticed by Berzelius, that the different forms of sulphur retain their peculiarities in combination. It is possible that the vapour of sulphur, as contained in sulphuretted hydrogen, may have an eq. volume greater than that of free sulphur, perhaps equal to that of hydrogen.

Berzelius proposes to call these different forms of elementary bodies *allotropic*. Thus sulphur may be said to exist either in its ordinary or in an allotropic state. Phosphorus and carbon appear to be capable of existing likewise in one or more allotropic forms.

It may here be observed, that the existence of these different forms in elementary bodies furnishes an additional argument against the notion of isomeric transmutation of elements. Here, in all probability, the very circumstances assumed as possible by the holders of that doctrine occur. The molecules of allotropic sulphur are no doubt different from those of ordinary sulphur; nay, in the dimorphism of sulphur this difference of molecules is almost rendered visible. But allotropic sulphur is still sulphur. In like manner, carbon, which is supposed, by a different grouping, to yield silicon, does actually exhibit a different grouping in the diamond, plumbago, and amorphous charcoal. But all these forms are still carbon.

The eq. of sulphur is 16·1; eq. vol. 16·66; symb. S.

The compounds of sulphur described in this section are composed as follows:—

	Sulphur.	Oxygen.	Equiv.	Formulæ.
Sulphurous Acid . .	16·1 or 1 eq.	+ 16 or 2 eq.	= 32·1	$S + 2O$ or SO_2
Sulphuric Acid . .	16·1 or 1 eq.	+ 24 or 3 eq.	= 40·1	$S + 3O$ or SO_3
Hyposulphurous Acid . .	32·2 or 2 eq.	+ 16 or 2 eq.	= 48·2	$2S + 2O$ or S_2O_2
Hyposulphuric Acid .	32·2 or 2 eq.	+ 40 or 5 eq.	= 72·2	$2S + 5O$ or S_2O_5
Sulphuretted Hyposulphuric Acid	48·3 or 3 eq.	+ 40 or 5 eq.	= 88·3	$3S + 5O$ or S_3O_5
Persulphuretted Hyposulphuric Acid . . .	64·4 or 4 eq.	+ 40 or 5 eq.	= 104·4	$4S + 5O$ or S_4O_5

Taking 16·66 as the eq. vol. of the vapour of sulphur, the weight of which is represented by 1·108, these compounds by measure are thus constituted:—

	Sulp.	Oxy.	Cond. into.	Densities.
Sulphurous Acid . .	16·66	+ 100	100	1·108 + 1·1025 = 2·2105
Sulphuric Acid . .	16·66	+ 150	100	1·108 + 1·6537 = 2·7617
Hyposulphurous Acid . .	33·33	+ 100	unknown.	
Hyposulphuric Acid .	33·33	+ 250	unknown.	
Sulphuretted Hyposulphuric Acid	49·99	+ 250	unknown.	
Persulphuretted Hyposulphuric Acid . . .	66·66	+ 250	unknown.	

SULPHUROUS ACID.

Hist. and Prep.—Discovered as a gas by Priestley. It is the sole product of the combustion of sulphur in air or dry oxygen gas, and is freely evolved, mixed with carbonic acid, when chips of wood, straw, cork, oil, or most other organic matters are heated in strong sulphuric acid, which yields oxygen to the carbon and hydrogen of those substances, and is thereby converted into sulphurous acid. Nearly all the metals, with the aid of heat, have a similar effect: one portion of the acid yields oxygen to the metal, and is thus reduced to sulphurous acid; while the metallic oxide, at the moment of its formation, unites with sulphuric acid. A very pure gas may thus be obtained by means of copper or mercury.

Prop.— Commonly gaseous, colourless, of a pungent suffocating odour, being that emitted by burning sulphur; taste, acid; sp. gr. 2·2105, and 100 C. I. at 60° and 30′ Bar. weigh 68·691 grains; it is liquid at 45° under the pressure of two atmospheres, and at 0° under that of one atmosphere. The gas extinguishes all burning bodies which are immersed into it, and is not inflammable. It does not support respiration, but causes violent irritation and spasm of the glottis; and even when diluted with air, it excites cough when inspired, and causes a peculiar uneasiness about the chest. Water, at 60° and 30′

Bar. dissolves 33 times its volume, the solution having the peculiar odour of the gas, and yielding it unchanged by ebullition. It has considerable bleaching properties: at first it reddens litmus paper, and then slowly bleaches it; but most vegetable colours, as of the rose and violet, are speedily removed by it without being first reddened. The colouring principle is not destroyed, but may be restored by a stronger acid, or by an alkali.

Davy proved that sulphurous acid gas contains exactly its own volume of oxygen (Elements, p. 273), and consequently the difference in the weights or sp. gr. of these gases ($2{\cdot}2105 - 1{\cdot}1025 = 1{\cdot}108$) gives the weight of sulphur combined with oxygen. The sulphur and oxygen are thus found to be in the ratio of 1·108 to 1·1025, or 16·1 to 16.

Liquid sulphurous acid is easily obtained by transmitting the dry pure gas through a glass tube surrounded by a freezing mixture of snow and salt. Its sp. gr. is 1·45; it boils at 14°, and from the rapidity of its evaporation causes intense cold; it conducts electricity (Kemp). When exposed to cold in the moist state, a crystalline solid is formed, which contains 20 per cent. of water, and probably consists of 1 eq. of the acid to 14 eq. of water.

Though sulphurous acid cannot be made to burn by the approach of flame, it has a very strong attraction for oxygen, uniting with it under favourable circumstances, and forming sulphuric acid. The presence of moisture is essential to this change. A mixture of sulphurous acid and oxygen gases, if quite dry, may be preserved over mercury for any length of time without chemical action; but if a little water be admitted, the sulphurous acid gradually unites with oxygen, and sulphuric acid is generated. Many of the chemical properties of sulphurous acid are owing to its affinity for oxygen. The solutions of metals which have a weak affinity for oxygen, such as gold, platinum, and mercury, are completely decomposed by it, those substances being precipitated in the metallic form. Nitric acid converts it instantly into sulphuric acid by yielding some of its oxygen. Peroxide of manganese causes a similar change, and is itself converted into protoxide of manganese, which unites with the resulting sulphuric acid.

Sulphurous acid gas may be passed through red-hot tubes without decomposition. Several substances which have a strong affinity for oxygen, such as hydrogen, carbon, and potassium, decompose it at the temperature of ignition.

Sulphurous acid combines with metallic oxides, and forms salts which are called *sulphites*, which are decomposed by sulphuric acid, and then emit the characteristic odour of sulphurous acid.

Its eq. is 32·1; eq. vol. $= 100$; symb. $S + 2O$, SO_2, or $\ddot{S}$.

SULPHURIC ACID.

Hist. and Prep.—Sulphuric acid, or *oil of vitriol* as it is often called, was discovered by Basil Valentine towards the close of the 15th century. It is procured for the purposes of commerce by two methods. One of these has been long pursued in the manufactory at Nordhausen in Germany, and consists in decomposing sulphate of oxide of iron (green vitriol) by heat. This salt contains 6 eq. of water of crystallization; and when strongly dried by the fire, it crumbles down into a white powder, which, according to Thomson, contains 1 eq. of water. On exposing this dried protosulphate to a red heat, its acid is wholly expelled, the greater part passing over unchanged into the receiver, in combination with the water of the salt. Part of the acid, however, is resolved by the strong heat employed in the distillation into sulphurous acid and oxygen. The former escapes as gas throughout the whole process; the latter only in the middle and latter stages, since, in the beginning of the distillation, it unites with the protoxide of iron. Peroxide of iron is the sole residue.

The acid, as procured by this process, is a dense, oily liquid of a brownish tint. It emits copious white vapours on exposure to the air, and is hence called *fuming sulphuric acid.* Its sp. gr. is 1·896 or 1·90. According to Thomson it consists of 80 parts or 2 eq. of anhydrous acid, and 9 parts or 1 eq. of water. On putting this acid into a glass retort, to which a receiver surrounded by snow is securely adapted, and heating it gently, a transparent colourless vapour passes over, which condenses into a white crystalline solid. This substance is pure anhydrous sulphuric acid, so called. Its eq. is 40·1; symb. $S + 3O$ or SO_3. It is tough and elastic; liquefies at 66° and boils at a temperature between 104° and 122°, forming, if no moisture is present, a transparent vapour. Exposed to the air, it unites with watery vapour, and flies off in the form of dense white fumes. When placed in contact with water, it hisses like red-hot iron, and is converted into oil of vitriol or hydrated sulphuric acid. Indeed the solid body SO_3 has no acid properties until it has combined with water. The residue of the distillation is no longer fuming, and is in every respect similar to the common acid of commerce.

The other process for forming sulphuric acid, which is practised in Britain and in most parts of the Continent, is by burning sulphur previously mixed with one-eighth of its weight of nitrate of potassa. The mixture is burned in a furnace so contrived that the current of air, which supports the combustion, conducts the gaseous products into a large leaden chamber, the bottom of which is covered to the depth of several inches with water. The nitric acid yields oxygen to a portion of sulphur, and converts it into sulphuric acid, which combines with the potassa of the nitre; while the greater part of the sulphur forms sulphurous acid by uniting with the oxygen of the air. The nitrous acid, in losing oxygen, is converted, partly perhaps into nitrous acid, but chiefly into binoxide of nitrogen, which, by mixing with air at the moment of its separation, gives rise to the red nitrous acid vapours. The gaseous substances, present in the leaden chamber, are therefore sulphurous and nitrous acids, atmospheric air, and watery vapour. The explanation of the mode in which these substances react on each other, so as to form sulphuric acid, was suggested by the experiments of Clément and Désormes (An. de Ch. lix.), and Davy (Elements, p. 276). When dry sulphurous acid gas and nitrous acid vapour are mixed together in a glass vessel quite free from moisture, no change ensues; but if a few drops of water be added, so as to fill the space with aqueous vapour, the white crystalline compound described in the section on hyponitrous acid is immediately produced. Clément and Désormes believed it to consist of sulphuric acid, binoxide of nitrogen, and water; and Davy, of sulphurous acid, nitrous acid, and water. But the observation that the same compound may be made with sulphuric and anhydrous nitrous acids, and that when decomposed by water both nitrous acid and binoxide of nitrogen are disengaged, led Gay-Lussac to the opinion which now seems to be fully substantiated by experiment. A consistent account may, therefore, be given of what really takes place within the leaden chambers.—The mutual reaction of humidity, sulphurous acid, and nitrous acid, gives rise to the crystalline compound of sulphuric acid, hyponitrous acid, and water; and when this solid falls into the water of the chamber, it is instantly decomposed, sulphuric acid is dissolved, and nitrous acid and binoxide of nitrogen escape with effervescence. The nitrous acid thus set free, as well as that reproduced by the binoxide uniting with the oxygen of the atmosphere, is again intermixed with sulphurous acid and humidity, and thus gives rise to a second portion of the crystalline solid, which undergoes the same change as the first. A certain portion of nitric acid is usually formed by the action of water on the nitrous acid; but the presence of sulphuric acid in that water tends to prevent the free decomposition of nitrous acid which pure water produces. Nay, when the water becomes pretty strongly acid, the nitric acid at first generated is reduced, by absorbed sulphurous acid, into the hyponitrous, which unites with sulphuric acid, and remains even after concentration: it is the cause of the evolution of binoxide of nitrogen which usually ensues when common oil of vitriol is diluted, the hyponitrous acid being then decomposed by the water (Dana). When the water of the chamber is sufficiently charged with acid, it is drawn off, and concentrated by evaporation. It hence appears that the oxygen, by which the sulphurous is converted into sulphuric acid, is in reality supplied by the air; that the combination is effected, not directly, but through the medium of nitrous acid; and that a small quantity of nitrous acid is sufficient for the production of a large quantity of sulphuric acid. The decomposition of the crystalline solid by water seems owing to the strong affinity of that liquid for sulphuric acid.

Besides hyponitrous acid, as above stated, it contains potassa, and the oxide of lead and sometimes iron, the first derived from the nitre employed in making it, and the two latter from the leaden chamber. To separate them, the acid should be distilled from a glass or platinum retort: the former may be safely used by putting into it some fragments of platinum leaf, which cause the acid to boil freely on applying heat, without danger of breaking the vessel. Arsenious acid, derived from arsenic in the sulphur used in the manufacture, has been lately detected in most of the oil of vitriol made in Germany; and from that source arsenic is introduced into preparations for which such acid is employed, as into phosphorus and hydrochloric acid. The arsenic is discovered by diluting with water and transmitting through the solution hydrosulphuric acid gas, which causes orpiment to be formed. The oil of vitriol may be purified from arsenious acid by adding a little hydrated peroxide of iron before distilling. The nitrous or hyponitrous acid generally present in smaller or larger proportions in the commercial sulphuric acid is highly injurious, since acid thus contaminated cannot be used for dissolving indigo, the colour of which is destroyed by the nitrous or hyponitrous acid. Various methods have been proposed for purifying it, such as heating the acid with a minimum of sugar until it no longer yields any indication of the presence of nitrous acid when tested by protosulphate of iron, as described under the head of nitric acid. If a slight excess of sugar should be employed, it blackens the acid, but if heated to the boiling point the sugar is entirely decomposed, and the carbon dissipated as carbonic acid along with a little sulphurous acid arising from the deoxidation of a portion of sulphuric acid by the carbon of the sugar. This method is not practically convenient, and perhaps the best way is to distil the acid, rejecting what passes over as long as it is found to contain nitrous acid. This method is not unattended with loss; but, as the acid cannot be purified from the other impurities without being distilled, it is on the whole the best.

Prop.—As obtained by the second process, pure sulphuric acid is a dense, colourless, oily fluid, which boils at 620° F., and has a sp. gr. in its most concentrated form of 1·847 or a little higher, never exceeding 1·850. Mitscherlich found the density of its vapour to be 3. It is one of the strongest acids with which chemists are acquainted, and when undiluted is powerfully corrosive. It decomposes all animal and vegetable substances by the aid of heat, causing deposition of charcoal and formation of water. It has a strong sour taste, and reddens litmus paper, even though greatly diluted. It unites with alkaline substances, and separates all other acids more or less completely from their combinations with the alkalies. Hydrated sulphuric acid, or oil of vitriol, is, in fact, the true sulphuric acid. The body above mentioned, under the name of anhydrous sulphuric acid, does not appear to possess acid properties at all until it comes in contact with water, when oil of vitriol is formed. It has generally been admitted that oil of vitriol is a compound of the anhydrous acid with water, $SO_3 + HO$; but it is at least equally probable that it is a compound of hydrogen, $H + SO_4$. It is true that the compound radical SO_4, here supposed to exist, cannot be obtained in a separate form; but this view notwithstanding appears to be preferable to the other. It happens, indeed, that the body SO_3 does exist, although its acid properties are more than doubtful; but in the case of nitric acid, which on the older view is $NO_5 + HO$, as oil of vitriol is $SO_3 + HO$, the supposed anhydrous nitric acid NO_5 is not known in a separate form any more than the compound radicals SO_4, or NO_6, the latter of which, with hydrogen, constitutes nitric acid on the new view, $H + NO_6$. The subject of the constitution of acids will be found more fully discussed in the general remarks on salts, prefixed to the description of that class of bodies.

In a very concentrated state it dissolves small quantities of sulphur, and acquires a blue, green, or brown tint. Tellurium and selenium are also sparingly dissolved, the former causing a crimson, and the latter a green colour. By dilution with water, these substances subside unchanged; but if heat is applied, they are oxidized at the expense of the acid, and sulphurous acid gas is disengaged. Charcoal also appears soluble to a small extent in sulphuric acid, communicating at first a pink, and then a dark reddish brown tint.

It has a very great affinity for water, and unites with it in every proportion. The combination takes place with production of intense heat. When four parts by weight of the acid are suddenly mixed with one of water, the temperature of the mixture rises, according to Ure, to 300°. By its attraction for water it causes the sudden liquefaction of snow; and if mixed with it in due proportion intense cold is generated. It absorbs watery vapour with avidity from the air, and on this account is employed in the process for freezing water by its own evaporation. Its action in destroying the texture of the skin, and in decomposing animal and vegetable substances in general, seems dependent on its affinity for water.

To ascertain the quantity of real acid present in liquid acid of different strengths, dilute a known weight of the acid moderately with water, and, while warm, add pure anhydrous carbonate of soda, until the solution is exactly neutral. Every 53·3 parts of carbonate of soda required to produce this effect correspond to 49·1 parts of oil of vitriol or real sulphuric acid. If minute precision is not desired, the strength of the acid may be estimated by its sp. gr. according to the table of Ure, inserted in the Appendix.

Sulphuric acid of commerce freezes at − 15°. Diluted with water so as to have a sp. gr. of 1·78 it crystallizes even above 32°, and remains in the solid state, according to Keir, till the temperature rises to 45°. This crystallizable acid is a definite hydrate, the formula of which is either $SO_3 + 2HO$, or $H,SO_4 + HO$; that is, oil of vitriol + 1 eq. of water. When mixed with rather more than its weight of water its freezing point is lowered to − 36°.

The composition of sulphuric acid as before given is founded on the observation of Gay-Lussac, that when the vapour of sulphuric acid is passed through a small porcelain tube heated to redness, it is resolved into two measures of sulphurous acid gas and one of oxygen. Berzelius has confirmed this conclusion by directly converting a known weight of sulphur into sulphuric acid.

Chemists possess an unerring test of the presence of sulphuric acid. If a solution of chloride of barium is added to a liquid containing sulphuric acid it causes a white precipitate, sulphate of baryta, which is characterized by its insolubility in acids and alkalies.

Sulphuric acid does not occur free in nature, except occasionally in the neighbourhood of volcanoes. In combination, particularly with lime and baryta, it is very abundant.

Its eq. is 49·1; symb. HO,SO_3, or H,SO_4.

Hyposulphurous Acid.—It may be formed either by digesting sulphur in a solution of any sulphite, or by transmitting a current of sulphurous acid into a solution of sulphuret of calcium or strontium. In the former case the sulphurous acid takes up an additional quantity of sulphur, and a salt of hyposulphurous acid is obtained; and, in the latter, the sulphurous acid gives part of its oxygen to the metal, and its remaining oxygen unites with sulphur. Three equivalents of sulphurous acid and two of sulphuret of calcium contain the elements for forming 2 eq. of hyposulphite of lime, 1 eq. of sulphur being deposited. A convenient solution for this purpose is made by boiling 3 parts of slaked lime and 1 of sulphur, with 20 parts of water, for one hour, and decanting the clear liquid from the undissolved portions; but when this solution is used, the deposit of sulphur is abundant. Herschel states that hyposulphurous acid may be formed by the action of sulphurous acid on iron filings; but the nature of the change is not well understood.

The salts of hyposulphurous acid were first described by Gay-Lussac (An. de Ch. lxxxv.) under the name of *Sulphuretted Sulphites.* Thomson, in his System of Chemistry, suggested that the acid of these salts might be regarded as a compound of one equivalent of sulphur and one of oxygen, and proposed for it the name of *hyposulphurous* acid; and the subsequent researches of Herschel (Phil. Journal, i. 8 and 396) accorded so entirely with this opinion, that it was universally adopted. But it appears from the experiments of Rose, that though the ratio of its elements is as 16 to 8, the equivalent of the acid, or the quantity required to neutralize 1 eq. of an alkali, is not 24, but 48; and hence that its smallest molecule must be formed of 2 atoms of sulphur united with 2 atoms of oxygen. (Pog. Ann. xxi. 431.) Its formula, if supposed anhydrous, is S_2O_2. Its hydrate, in all probability, is HO,S_2O_2, or H,S_2O_3.

Prop.—It cannot exist permanently in a free state. On decomposing a hyposulphite by any stronger acid, such as the sulphuric or hydrochloric, the hyposulphurous acid, at the moment of quitting the base, resolves itself into sulphurous acid and sulphur. Herschel succeeded in obtaining free hyposulphurous acid by adding a slight excess of sulphuric acid to a dilute solution of hyposulphite of strontia; but its decomposition very soon took place, even at common temperatures, and was instantly effected by heat. Most of the hyposulphites are soluble in water, and have a bitter taste. The solution precipitates the nitrates of the oxides of silver and mercury black, as sulphuret of the metals; and salts of baryta and oxide of lead are thrown down as white insoluble hyposulphites of those bases. That of baryta is soluble without decomposition in water acidulated with hydrochloric acid. The solution of all the neutral hyposulphites has the peculiar property of dissolving recently precipitated chloride of silver in large quantity, and forming with it a liquid of an exceedingly sweet taste.

Hyposulphuric Acid.—It was discovered in 1819 by Welter and Gay-Lussac (An. de Ch. et Ph. x.), and is formed by transmitting a current of sulphurous acid gas through water containing peroxide of manganese in fine powder; when, by a new arrangement of their elements,

$$\underset{2SO_2}{\text{2 eq. Sulp. Acid}} \text{ and } \underset{MnO_2}{\text{1 eq. Perox. Mang.}} \text{ yield } \underset{MnO}{\text{1 eq. Protox. Mang.}} \text{ and } \underset{S_2O_5}{\text{1 eq. Hyposulph. Acid,}}$$

hyposulphate of protoxide of manganese remaining in solution. During the action heat is freely evolved, and, in consequence, sulphuric acid is also generated; but if the peroxide of manganese be pure, and the materials kept cool, the formation of sulphuric acid is almost completely prevented. To the liquid, after filtration, a solution of pure baryta or sulphuret of barium in slight excess is added, whereby the manganese is thrown down as an oxide or sulphuret, sulphuric acid as sulphate of baryta, and a solution of hyposulphate of baryta is obtained: the excess of baryta is got rid of by a free current of carbonic acid gas, and then heating the solution. The hyposulphate of baryta crystallizes by evaporation; and, on decomposing a solution of that salt by a quantity of sulphuric acid exactly sufficient for precipitating the baryta, the hyposulphuric acid is left in solution.

Prop.—Taste sour; distinct acid reaction; neutralizes alkalies; inodorous, and thus distinguished from sulphurous acid; forms soluble salts with baryta, strontia, lime, and oxide of lead, by which it is distinguished from sulphuric acid. It cannot be obtained free from water. Its solution, if confined with a vessel of sulphuric acid under the exhausted receiver of an air-pump, may be concentrated till it has a density of 1·347; but if an attempt is made to condense it still further, the acid is decomposed, sulphurous acid gas escapes, and sulphuric acid remains in solution. A similar change is still more readily produced if the evaporation is conducted by heat.

Welter and Gay-Lussac analyzed hyposulphuric acid by exposing neutral hyposulphate of baryta to heat. At a temperature a little above 212° this salt suffers complete decomposition; sulphurous acid gas is disengaged, and neutral sulphate of baryta is obtained. It was thus ascertained that 72 grains of hyposulphuric acid yield 32 grains of sulphurous, and 40 of sulphuric acid; from which it is inferred that hyposulphuric acid is composed either of an equivalent of each of those acids combined with each other, or of 2 eq. of sulphur and 5 of oxygen.

Sulphuretted Hyposulphuric Acid.—Langlois observed that when sulphur is boiled in a solution of bisulphite of potassa a salt is obtained, the acid of which he procured in a separate form, although diluted with water. He took it at first for hyposulphurous acid; but a careful analysis proved that it contained the elements of 1 eq. hyposulphuric acid and 1 eq. sulphur. Hence the name above given to it.

The theory of its formation is still obscure; but it is a distinct acid, and forms crystallizable salts, which are distinguished by the action of heat upon them. When ignited in close vessels, they give off 1 eq. of sulphur and 1 eq. of sulphurous acid, while a neutral sulphate is left. This is easily explained by the formula of these salts, which is $MO + S_3O_5 = (MO,SO_3) + SO_2 + S$. The formula of the hydrated acid is HO,S_3O_5, or H,S_3O_6.

Persulphuretted Hyposulphuric Acid.—This is another new acid, discovered by Fordos and Gélis. Like the preceding acid, which it much resembles, it is more permanent in the uncombined form than hyposulphurous acid. It forms well-defined crystallized salts, which are characterized by giving off, when heated in close vessels, 1 eq. of sulphurous acid, and 2 eq. of sulphur, while 1 eq. of a neutral sulphate is left. The general formula of its salts is $MO + S_4O_5 = (MO,SO_3) + SO_2 + S_2$. The formula of the hydrated acid is HO,S_4O_5, or H,S_4O_6.

The interest attached to the two last-described acids arises from the evidence they afford of the variety of proportions in which their elements can unite. The proportions are unusual; but it is probable that many similar acids will be discovered.

Having now described the compounds of sulphur and oxygen, it is proper to point out that they are all acids, and that all of them, except sulphurous acid, require the addition of the elements of water, that is, of hydrogen, in order to exist as free acids. Hence, we are inclined to apply to all but sulphurous acid the theory which considers all acids as hydrogen acids. It is worthy of remark, that while the so-called anhydrous sulphuric acid has no acid properties, those of sulphurous acid are not well marked. We may consider sulphurous acid, in a manner, as the true basis or radical of all the others; and, if we view it as an acid, we shall find that it undergoes no change in its neutralizing power by being converted into the others. It is as if the radical of the sulphites were changed by the addition of new matter, without its power of saturation being affected. Thus, we have, in the

Sulphites . .	$M + SO_3$
Sulphates . .	$M + (SO_3 + O)$
Hyposulphites . .	$M + (SO_3 + S)$
Hyposulphates .	$M + (SO_3 + SO_3)$
Acid of Langlois .	$M + (SO_3 + SO_3 + S)$
Acid of Fordos and Gélis	$M + (SO_3 + SO_3 + S + S)$.

Admitting, therefore, SO_3 as the radical of the sulphites, we see that all the additions made to that radical have not affected the neutralizing power, which is still represented by 1 eq. of M or of H. Even the addition of other elements does not alter the power of saturation; for two acids have been discovered, the nitrosulphuric by Pelouze, and the chlorosulphuric by Regnault, the salts of which are represented as follows:—

Nitrosulphates . . . $M + (SO_3 + NO_2)$
Chlorosulphates . . . $M + (SO_3 + Cl)$.

These facts furnish a strong support to the view, according to which the neutralizing power of acids is measured by, and depends upon, the amount of hydrogen, replaceable by metals, which they contain.

SECTION VIII.

PHOSPHORUS.

Hist. and Prep.—Phosphorus (*φωσφόρος*, from *φῶς light* and *φέρειν to carry*), so called from its property of shining in the dark, was discovered about the year 1669 by Brandt, an alchemist of Hamburgh. It was originally prepared from urine; but Scheele, after Gahn's discovery of bones containing phosphate of lime, extracted it from that source. The bones are first ignited in an open fire till they become white, so as to destroy their animal matter, and burn away the charcoal derived from it, in which state they contain nearly 4-5ths of phosphate of lime. They are then reduced to a fine powder, and digested for a day or two with rather more than half their weight of strong sulphuric acid, with the addition of so much water as will give the consistence of a thin paste. Decomposition of the phosphate of lime is thus effected, and two new salts formed, the sparingly soluble sulphate and a soluble superphosphate of lime. The latter is dissolved in warm water, and the solution, after being separated by filtration from the sulphate of lime, is evaporated to the consistence of syrup, mixed with a fourth of its weight of powdered charcoal, and strongly heated in an earthen retort well luted with clay. The beak of the retort is put into water, in which the phosphorus, as its vapour passes over, is condensed. When first obtained it is usually of a reddish brown colour, owing to the presence of phosphuret of carbon formed during the process. It may be purified by fusion in hot water, and being pressed while liquid through chamois leather, or by a second distillation.

In this process the oxygen of that part of the phosphoric acid which constitutes the superphosphate, unites with charcoal, giving rise to carbonic acid and carbonic oxide gases; and phosphate of lime in the state of bone earth, together with redundant charcoal, remains in the retort. The lime acts an important part in fixing the phosphoric acid, which if not so combined would distil over before the heat was high enough for its decomposition. In extracting phosphorus from urine, the phosphoric acid should be thrown down by acetate of the oxide of lead, and the insoluble salt converted by the action of sulphuric acid into the superphosphate, which is decomposed by charcoal as in the former process.

Prop.—When pure, transparent and almost colourless. At common temperatures it is a soft solid, of sp. gr. 1·77; is easily cut with a knife, and the cut surface has a waxy lustre: at 108° it fuses, and at 550° is converted into vapour, which according to Dumas has a sp. gr. of 4·355. It is soluble by the aid of heat in naphtha, in fixed and volatile oils, in the chloride of sulphur, sulphuret of carbon, and sulphuret of phosphorus. On its cooling from solution in the latter, Mitscherlich obtained it in regular dodecahedral crystals. By the fusion and slow cooling of a large quantity of phosphorus, M. Frantween has obtained very fine crystals of an octohedral form, and as large as a cherry-stone. Thenard has remarked that when phosphorus is fused at 150°, and suddenly cooled by being plunged into cold water, it appears black; but by fusion and slow cooling it recovers its original aspect. This seems to point out that phosphorus, like sulphur, can exist in more forms than one. The black phosphorus is probably allotropic.

It is exceedingly inflammable. Exposed to the air at common temperatures, it undergoes slow combustion, emits a white vapour of a peculiar alliaceous odour, appears distinctly luminous in the dark, and is gradually consumed. On this account, phosphorus should always be kept under water. The disappearance of oxygen which accompanies these changes is shewn by putting a stick of phosphorus in a jar full of air, inverted over water. The volume of the gas gradually diminishes; and if the temperature of the air is at 60°, the whole of the oxygen will be withdrawn in the course of 12 or 24 hours. The residue is nitrogen gas, containing about 1-40th of its bulk of the vapour of phosphorus. It is remarkable that the slow combustion of phosphorus does not take place in pure oxygen, unless its temperature be about 80°. But if the oxygen be diluted with nitrogen, hydrogen, or carbonic acid gases, the oxidation occurs at 60°; and it takes place at temperatures still lower in a vessel of pure oxygen, rarefied by diminished pressure. Mr. Graham finds that the presence of certain gaseous substances, even in minute quantity, has a remarkable effect in preventing the slow combustion of phosphorus: thus at 66° it is entirely prevented by the presence (Quar. Jour. of Science, N. S., vi. 83)

	Volumes of Air.
of 1 volume of Olefiant Gas in	450
1 ditto of Vapour of Sulphuric Ether in	150
1 ditto of Vapour of Naphtha in	1820
1 ditto of Vapour of Oil of Turpentine in	4444,

and by an equally slight impregnation of the vapour of the other essential oils. Their influence is not confined to low temperatures. Phosphorus becomes faintly luminous in the dark, in mixtures of

1 volume of Air	and 1 volume of Olefiant Gas at	200° F.
1	and 1 ditto of Vapour of Ether at	215°
111	and 1 ditto of Vapour of Naphtha at	170°
156	and 1 ditto of Vapour of Turpentine at	186°.

It may be sublimed at its boiling temperature, in air containing a considerable proportion of the vapour of oil of turpentine, without diminishing the quantity of oxygen present, provided the heat be gradually and uniformly applied. Mr. Graham has also remarked that the oxidation of phosphorus in the air is promoted by the presence of hydrochloric acid gas.

A very slight degree of heat is sufficient to inflame phosphorus in the open air. Gentle pressure between the fingers, friction, or a temperature not much above its point of fusion, kindles it readily. It burns rapidly even in the air, emitting a splendid white light, and causing intense heat. Its combustion is far more rapid in oxygen gas, and the light proportionally more vivid.

When phosphorus is kept for a long time under water, especially if exposed to light, its surface acquires a thin coating of white matter, which some have described as an oxide, and others as a hydrate of phosphorus. It seems according to Rose to be neither an oxide nor a hydrate, but phosphorus in a peculiar mechanical state, which deprives it of its usual action upon light, and renders it opaque. This is possibly another allotropic modification of phosphorus. (Pog. Annalen, xxvii. 565.)

Repeated researches by Berzelius have shewn that the oxygen in phosphorous and phosphoric acids is in the ratio of 3 to 5, a result conformable to experiments on the same subject by Dulong, and admitted by most chemists. It is hence inferred that the smallest molecule of phosphoric acid contains 5 atoms of oxygen. Also Berzelius finds that 31·4 parts of phosphorus require 40 of oxygen for forming phosphoric acid: if this acid consist of 1 atom of phosphorus and 5 atoms of oxygen, 31·4 will represent 1 atom of phosphorus; or if the acid contain 2 atoms to 5, the atom of phosphorus will be half 31·4 or 15·7. Chemists seem now generally disposed to adopt the former view, although the latter has long been prevalent. As I can see no good reason for halving the eq. of phosphorus, I shall adopt the larger number.

Its equivalent is therefore 31·4; eq. vol. = 25; symb. P.

The compounds of phosphorus described in this section are the following:—

	Phosp.	Oxygen.	Equiv.	Formulæ.
Oxide of Phosphorus . .	94·2 or 3 eq.	16 or 2 eq. =	110·2	$3P + 2O$ or P_3O_2
Hypophosphorous Acid .	31·4 or 1 eq.	8 or 1 eq. =	39·4	$P + O$ or PO.
Phosphorous Acid . .	31·4 or 1 eq.	24 or 3 eq. =	55·4	$P + 3O$ or PO_3
Phosphoric Acid . .	31·4 or 1 eq.	40 or 5 eq. =	71·4	$P + 5O$ or PO_5

COMPOUNDS OF OXYGEN AND PHOSPHORUS.

Oxide.—When a jet of oxygen gas is thrown upon phosphorus while in fusion under hot water, combustion ensues, phosphoric acid is formed, and a number of red particles collect, which have been examined by M. Pelouze, who has shewn them to be an oxide of phosphorus. The red matter left when phosphorus is burned is probably of the same nature.

This, the only known oxide of phosphorus, is of a red colour, without taste or odour, and is insoluble in water, ether, alcohol, and oil. It is permanent in the air, even at 662° F., but takes fire at a low red heat. Heated to redness in a tube, phosphorus is expelled, and metaphosphoric acid remains. It takes fire in chlorine gas, and is rapidly oxidized by nitric acid. It does not appear to possess any alkaline character. (An. de Ch. et Ph. 1·83.) Its equivalent is 55·1; symb. $3P + 2O$ or P_3O_2. This is the only compound of phosphorus and oxygen, the composition of which seems to favour the halving of the eq. of phosphorus. Adopting the eq. 15·7, the formula of the oxide is P_3O, while with the eq. 31·4 its formula is P_3O_2. Both of these are unusual formulæ, but we cannot view this compound as fully known.

Hypophosphorous Acid.—This acid was discovered in 1816 by Dulong. (An. de Ch. et Ph. ii.) When water acts upon the phosphuret of barium the elements of both enter into a new arrangement, giving rise to phosphuretted hydrogen, phosphoric acid, hypophosphorous acid, and baryta. The former escapes in the form of gas, and the two latter combine with the baryta. Hypophosphite of baryta, being soluble, dissolves in the water, and may consequently be separated by filtration from the phosphate of baryta, which is insoluble. On adding a sufficient quantity of sulphuric acid for precipitating the baryta, hypophosphorous acid is obtained in a free state, and on evaporating the solution, a viscid liquor remains, highly acid and even crystallizable, which is a hydrate of hypophosphorous acid. When exposed to heat in close vessels, it undergoes the same kind of change as hydrated phosphorous acid.

Prop.—It is a powerful deoxidizing agent. It unites with alkaline bases; and it is remarkable that all its salts are soluble in water. The hypophosphites of potassa, soda, and ammonia dissolve in every proportion in rectified alcohol; and hypophosphite of potassa is even more deliquescent than chloride of calcium. They are all decomposed by heat, and yield the same products as the acid itself. They are conveniently prepared by precipitating hypophosphite of baryta, strontia, or lime, with the alkaline carbonates; or by directly neutralizing these carbonates with hypophosphorous acid. The hypophosphite of baryta, strontia, and lime are formed by boiling these earths in the caustic state in water together with fragments of phosphorus. The same change occurs as during the action of water on phosphuret of barium. The composition of this acid, as above stated, is on the authority of Rose. (Poggen. Annalen, ix. 367.) Its eq. is 39·4; symb. $P + O$, $\dot{P}$, or PO. The hydrate is probably HO,PO.

Phosphorous Acid.—Prep.—When phosphorus is burned in air highly rarefied, imperfect oxidation ensues, and metaphosphoric and phosphorous acids are generated, the latter being obtained in the form of a white volatile powder. It may be procured more conveniently by subliming phosphorus through powdered bichloride of mercury contained in a glass tube; when a limpid liquid comes over, which is a compound of chlorine and phosphorus. (Davy's Elements, p. 288.) This substance and water mutually decompose each other: the hydrogen of water unites with the chlorine, and forms hydrochloric acid; while the oxygen attaches itself to the phosphorus, and thus phosphorous acid is produced. The solution is then evaporated to the consistence of syrup to expel the hydrochloric acid; and the residue, which is hydrate of phosphorous acid, becomes a crystalline solid on cooling. It is also generated during the slow oxidation of phosphorus in atmospheric air. The product attracts moisture from the air, and forms an oil-like liquid. Dulong thinks that a distinct acid is produced in this case, which he calls *phosphatic acid;* but the opinion of Davy, that it is merely a mixture of phosphoric and phosphorous acids, is, in my opinion, perfectly correct.

Prop.—When obtained by the first process, it is anhydrous. Heated in the open air, it takes fire and forms metaphosphoric acid; but in close vessels it is resolved into metaphosphoric acid and phosphorus. The action of the hydrate under the latter circumstances is different, owing to the reaction of the elements of the water and acid, by which metaphosphoric acid and a gaseous compound of phosphorus and hydrogen are produced. The nature of this gas will be more particularly noticed in the section on phosphuretted hydrogen. Phosphorous acid dissolves readily in water, has a sour taste, and smells somewhat like garlic. It unites with alkalies, and forms salts which are termed *phosphites*. The solution of phosphorous acid absorbs oxygen slowly from air, and is converted into phosphoric acid. From its tendency to unite with an additional quantity of oxygen, it is a powerful deoxidizing agent; and hence, like sulphurous acid, precipitates mercury, silver, platinum, and gold, from their saline combinations in the metallic form. Nitric acid converts it into phosphoric acid.

Its eq. is 55·4; symb. $P + 3O$, $\dddot{P}$, or PO_3. The crystallized hydrate is $3HO,PO_3$.

Phosphoric Acid.—There are four compounds generally included under this name; the anhydrous acid, and the three acids often called metaphosphoric, pyro-phosphoric, and common phosphoric acids. According to some, these are merely three hydrates of the dry acid; but although any one of the three may be readily converted into either of the others, they appear fully entitled to rank as distinct acids, since they not only differ in properties when uncombined, but form distinct and peculiar salts with bases.

1. *Anhydrous Phosphoric Acid.*—This compound can only be obtained by burning phosphorus in dry air or oxygen gas. It may be easily procured by burning phosphorus, placed in a little cup, which stands on a clean brass plate, under a large bell jar full of dry air. The acid collects on the plate as a white mass exactly like snow. By using a tubulated jar, connected with a reservoir of dry oxygen, and having a tube open at both ends passing through the cork, beside the tube which conveys the gas, through which phosphorus may be introduced at pleasure, and by carefully regulating the current of oxygen, large quantities of the acid may be easily obtained.

It is exceedingly deliquescent, and must therefore be instantly put up in well-closed phials or hermetically sealed tubes, if it is to be preserved anhydrous. When thrown into water it hisses like red-hot iron, and is soon dissolved, forming at first a solution of metaphosphoric or monobasic phosphoric acid, which passes into bibasic and tribasic acid, slowly in the cold, rapidly if boiled.

There is no evidence that anhydrous phosphoric acid, any more than anhydrous sulphuric acid, possesses acid properties before it has combined with the elements of water. It is true that it tastes intensely sour, but it cannot be tasted without being moistened with the saliva, and thus, *pro tanto*, converted into monobasic acid. On the whole, this body is to be viewed as belonging to the same class as the anhydrous sulphuric acid, and not, therefore, a true acid, in the strict sense of the word. Its eq. is 71·4: symb. $P + 5O$ or PO_5.

2. *Monobasic Phosphoric Acid.* Syn. *Metaphosphoric Acid.*—This acid is obtained when any solution of common or tribasic phosphoric acid is evaporated to a syrup and ignited. Under these circumstances, the whole of the water is expelled, except 1 eq., the elements of which cannot be driven off by heat, when once they have combined with those of the anhydrous acid. The preparation of the tribasic acid will be given below. The monobasic acid is also obtained when phosphate of ammonia is heated until the ammonia is entirely expelled. But this process is only adapted for the small scale.

When obtained as above, the monobasic acid appears as a very fusible, colourless, transparent glass, called glacial-phosphoric acid, very acid and soluble in water, being deliquescent in the air. Its composition is represented by the formula HO,PO_5, or H,PO_6. The water, or elements of water, cannot be expelled by heat, the whole acid subliming if strongly heated in close vessels. In the open fire it volatilizes rapidly at a temperature even below ignition.

The solution of this acid in water is not permanent, gradually passing into bibasic and tribasic acids. But if made in the cold, it retains for some time its peculiar characters. It coagulates albumen, and causes in the salts of baryta and oxide of silver, bulky gelatinous grayish-white precipitates of the monobasic phosphates of these bases.

The most marked character of this acid is pointed out in its name. It is that of uniting with 1 eq. of water, or of a fixed base. This will be more fully discussed hereafter. Its eq. is 80·4; symb. HO,PO_5 or H,PO_6.

3. *Bibasic Phosphoric Acid.* Syn. *Pyrophosphoric Acid* of Clark, its discoverer.—It may be obtained by exposing tribasic phosphoric acid for some time to a heat not exceeding 415°. Its general characters resemble those of the other phosphoric acids; but when neutralized by ammonia and mixed with nitrate of oxide of silver it yields a snow-white granular precipitate, bibasic phosphate of that oxide, by which it is distinguished from the tribasic and monobasic acids. In solution with cold water this acid passes gradually, and at a boiling temperature rapidly, into tribasic phosphoric acid. Its salts, while neutral, are very permanent; but when boiled with any of the stronger acids in water, they are quickly converted more or less completely into tribasic phosphates.

Pyrophosphoric acid is remarkable for its tendency to unite with two equivalents of a base. Its aqueous solution probably contains a dipyrophosphate of water, that is, 1 eq. of the acid with 2 eq. of water, expressed by $2HO + PO_5$, or $2HO,PO_5$. This basic water is readily displaced by 2 eq. of stronger bases, such as soda; or if 1 eq. only of soda be added, then the soda and water together make up the 2 eq. of base, the formula of the salt being NaO,HO,PO_5. The readiest mode of obtaining a pyrophosphate is to heat phosphoric acid with any fixed base in the ratio of one to two of their equivalents. This was done by Dr. Clark in the experiments by which he established the existence of pyrophosphoric acid. (Brewster's Journal, vii. 298.) Phosphate of soda is a compound of 1 eq. phosphoric acid, 2 eq. soda, 1 eq. basic water, and 24 eq. water of crystallization, its formula being $2NaO,HO,PO_5 + 24HO$: on drying this salt its water of crystallization is expelled, there remains $2NaO,HO,PO_5$, which is still a phosphate, but on heating to redness the basic water is expelled, and $2NaO,PO_5$, pyrophosphate of soda, remains. By being forced to unite with 2 eq. of base, the acid acquires a disposition to do so on all occasions.

Its eq. is 89·4; symb. $2HO,PO_5$, or H_2,PO_7.

4. *Tribasic Phosphoric Acid.* Syn. *Common Phosphoric Acid.*— One of the best modes for procuring it, is to oxidize phosphorus by strong nitric acid; but in this process care is necessary, as the action is sometimes very violent, and the escape of binoxide of nitrogen gas ungovernably rapid. It is safely conducted by adding fragments of phosphorus, or the so-called phosphatic acid, to strong nitric acid contained in a platinum crucible partially closed by its cover. Gentle heat is applied so as to commence, and, when necessary, to maintain moderate effervescence; and when one portion of phosphorus disappears, another is added, till the whole of the nitric acid is exhausted. The solution is then evaporated to dryness, and exposed to a red heat to expel the last traces of nitric acid. This should always be done in vessels of platinum, since phosphoric acid acts chemically upon those of glass or porcelain, and is thereby rendered impure. In this case, as in some other instances of the oxidation of combustibles by nitric acid, water is decomposed; and while its oxygen unites with phosphorus, its hydrogen combines with nitrogen of the nitric acid. A portion of ammonia, thus generated, is expelled by heat in the last part of the process.

Phosphoric acid may be prepared at a much cheaper rate from bones. For this purpose, superphosphate of lime, obtained in the way already described, should be boiled for a few minutes with excess of carbonate of ammonia. The lime is thus precipitated as a phosphate, and the solution contains phosphate, together with a little sulphate, of ammonia. The liquid, after filtration, is evaporated to dryness, and then ignited in a platinum crucible, by which means the ammonia and sulphuric acid are expelled.

In both the foregoing processes phosphoric acid exists only in solution; for on heating to redness, in order to expel ammonia in the one case, and nitric acid in the other, metaphosphoric acid is generated. To reproduce the phosphoric acid, the residue in the crucible requires to be dissolved in water and boiled for a few minutes.

The following process, which Gregory has lately proposed, enables us readily to obtain pure phosphoric acid from bones, without the use of ammonia, which is found very troublesome except on a small scale. It is a modification of a method proposed some years since by Liebig.

To the syrupy solution of superphosphate of lime, described in the praperation of phosphorus, sulphuric acid is added, in the proportion of about one-tenth of that originally used to decompose the burnt bones. The whole mass becomes nearly solid from the separation of sulphate of lime. It is diluted with cold water, and thrown on a cloth filter, where the sulphate is washed with cold water until it passes through nearly tasteless. The filtered solution, with the washings, is then again concentrated and filtered or decanted off from some sulphate of lime which, having been dissolved by the water used in washing, separates during the evaporation. The filtered liquid is again evaporated to a syrup, and a small portion tested by the addition of sulphuric acid. If any sulphate of lime is formed, the whole of the lime has not been removed, and a little sulphuric acid is to be added, and the filtration, &c. repeated. When the syrupy solution no longer becomes turbid on the addition of sulphuric acid, the whole of the lime has been removed, and the liquid contains, besides the phosphoric acid and the excess of sulphuric acid, only the phosphate of magnesia contained in the bones, and, as has lately been ascertained, a small proportion of soda, also derived from the bones.

It is now heated in a covered platinum crucible as long as the vapours of sulphuric acid are expelled, and there is left a transparent glacial acid, still, however, contaminated with magnesia and soda. If the process has been carefully performed not a trace of lime is left. The glass is now dissolved in water, which, with the aid of heat, dissolves it slowly but completely. The solution is next evaporated, in a platinum vessel, until so much water has been expelled that its temperature rises to 600°. At this point it suddenly becomes turbid from the separation of an insoluble salt. This salt Gregory analyzed, and took for a compound of 3 eq. of magnesia and 2 eq. of phosphoric acid, the existence of soda in the bones not being previously known. But this salt has been found by experiments made in Baron Liebig's laboratory by Mr. Maundrell, to be a phosphate of magnesia and soda. This result Gregory has confirmed. The heat of 600° should be kept up for a quarter of an hour or half an hour, when the whole of the salt will most probably separate; but if, when the soluble part has been separated from the insoluble, the filtered liquid, evaporated and heated to 600°, again grows turbid, the operation must be repeated till that effect is no longer to be perceived. The filtered liquid is now a solution of pure phosphoric acid, and when evaporated and ignited in a covered platinum crucible yields a perfectly colourless and transparent glass of monobasic acid, far more easily dissolved in water than the impure glacial acid obtained in the first stage of the process.

Prop.—Tribasic phosphoric acid is colourless, intensely sour to the taste, reddens litmus strongly, and neutralizes alkalies; but it does not destroy the texture of the skin, like sulphuric and nitric acids. Its solution may be evaporated at a temperature of 300° without decomposition, and when thus concentrated it assumes a dark colour, is as thick as treacle when cold, and consists of 71·4 parts or 1 eq. of phosphoric acid and 27 parts or 3 eq. of water. Mr. Graham obtained this hydrate in thin crystalline plates, which were extremely deliquescent, by keeping it for seven days *in vacuo* along with sulphuric acid. On heating this hydrate for several days to 415°, it lost nearly two-thirds of an equivalent of water, and then principally consisted of pyrophosphoric acid with two equivalents of water. At a still higher temperature metaphosphoric acid began to be formed; and at a red heat the conversion was complete. But after ignition it still contains water, amounting, according to Rose, to 9·44 per cent., which is rather more than an equivalent of water to one of metaphosphoric acid.

Phosphoric acid is remarkable for its tendency to unite with alkaline bases, in such proportions that the oxygen of the base and of the acid is as 3 to 5; or, in other words, it is prone to form salts, in which one equivalent of acid is combined with three equivalents of base. It manifests the same character in regard to water, and ceases to be phosphoric acid unless three equivalents of water to one of acid are present: it even appears that the water acts the part of a base, hence called *basic* water, and that the aqueous solution is not a mere solution of phosphoric acid, but of triphosphate of water, a sort of salt composed of one equivalent of acid and three equivalents of water. Part of this basic water enters along with soda into the constitution of two of the tribasic phosphates of soda, the water and soda together forming the three equivalents of base required by one equivalent of the acid. This point will be more fully described in the history of the Phosphates.

When phosphoric acid is neutralized by ammonia and mixed with nitrate of oxide of silver, the yellow phosphate of that oxide subsides; a character by which it is distinguished from the bibasic and tribasic acids, as well as from all other acids except the arsenious. A certain test between phosphoric and arsenious acids is, that the former is neither changed in colour nor precipitated when a stream of hydrosulphate acid gas is transmitted through it; while the latter, with the required precautions, first acquires a yellow tint, and then yields a yellow precipitate.

Its eq. is 98·4; symb. $3HO,PO_5$ or H_3,PO_8.

From the above description of the different phosphoric acids, the reader will perceive that the properties of the monobasic, bibasic, and tribasic acids are quite distinct. If, with some authors, we regard them merely as different hydrates of the anhydrous acid, we have no means of accounting for the fact of their uniting respectively with 1, 2, or 3 eqs. of base. To say that when dry phosphoric acid is combined with 1, 2, or 3 eqs. of water it has acquired a tendency to unite with 1, 2, or 3 eqs. of base, is merely stating the fact in other words. Besides, we are acquainted with three hydrates of dry sulphuric acid, in which no such tendency appears. They all, when neutralized, yield monobasic sulphates. Some further explanation is obviously required; and we obtain what is, at all events, a more satisfactory one, if we admit the doctrine of hydrogen acids with compound radicals containing oxygen, and the existence of polybasic acids.

In an admirable paper on the constitution of the organic acids, Liebig has shewn, that, if we adopt the view first suggested by Davy, and afterwards by Dulong, namely, that the hydrated acids, as well as the hydracids, are all compounds of hydrogen, we can easily understand how the three forms of phosphoric acid differ from each other. On this view, just as hydrochloric acid is H,Cl, hydrated sulphuric acid is H,SO_4. In like manner, metaphosphoric acid is H,PO_6; pyrophosphoric acid is H_2,PO_7, and common phosphoric acid is H_3,PO_8. They are thus distinct compounds, as is evident from the differences among their salts. When the hydrogen in them is replaced, equivalent for equivalent, by a metal, a salt is formed; and we thus see how the salts of metaphosphoric acid contain 1 eq. of metal, those of pyrophosphoric acid 2 eq., and those of common phosphoric acid 3 eq. of metal. The first is a monobasic acid, the second a bibasic, and the third a tribasic acid. The memoir of Liebig just referred to (Ann. der Pharm. vol. xxvi.) has placed beyond question the existence of polybasic acids; that is, acids which combine with more than one equivalent of base to form neutral salts. This subject will be more fully discussed hereafter, in the section on Salts.

SECTION IX.

BORON.

Hist. and Prep.—Sir H. Davy discovered the existence of *Boron* in 1807 by exposing boracic acid to the action of a powerful galvanic battery; but he did not obtain a sufficient supply of it for determining its properties. Gay-Lussac and Thenard* procured it in greater quantity in 1808 by heating boracic acid with potassium. The boracic acid is by this means deprived of its oxygen, and boron is set free. The easiest and most economical method of preparing this substance, according to Berzelius, is to decompose borofluoride of potassium or sodium by means of potassium. (Annals of Philosophy, xxvi. 128.)

Prop.—It is a dark olive-coloured substance, which has neither taste nor smell, and is a non-conductor of electricity. It is insoluble in water, alcohol, ether, and oils. It does not decompose water, whether hot or cold. It bears intense heat in close vessels, without fusing or undergoing any other change except a slight decrease of density. Its sp. gr. is about twice as great as that of water. It may be exposed to the atmosphere at common temperatures without change; but if heated to 600°, it suddenly takes fire, oxygen gas disappears, and boracic acid is generated. It is very difficult to oxidize all the boron by burning, because the boracic acid fuses at the moment of being formed, and by glazing the surface of the unburned boron protects it from oxidation. It also passes into boracic acid when heated with nitric acid, or with any substance that yields oxygen with facility.

According to the experiments of Davy and Berzelius, boron in burning unites with 68 per cent. of oxygen; and the latter, from the composition of borax, estimates the oxygen in boracic acid at 68·8 per cent. In this, as in some other cases, where a combustible unites with oxygen in one proportion only, it is difficult with any certainty to assign the true atomic constitution of the compound. Boracic acid may be a compound of boron and oxygen in the ratio of 1 atom to 1 atom, in that of 1 to 2 as supposed by Thomson, or of 1 to 3. When dry boracic acid is heated with charcoal in chlorine gas, it is decomposed, and two volumes of chloride of boron and three of carbonic oxide gas are produced. The latter contains 1½ volumes of oxygen, and the former has been proved by Dumas to be composed of 3 volumes of chlorine united with 1 volume of the vapour of boron, the density of which is estimated at ·751, its eq. vol. being 100. From this it may be deduced that the constitution of boracic acid is BO_3, which has also been recently adopted by Berzelius (Pog. An. xxiv. 561). Hence its eq. is 10·9; eq. vol. = 100; symb. B.

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* Recherches Physico-Chimiques, vol. i.

Boracic Acid.—Hist. and Prep.—This is the only known compound of boron and oxygen. As a natural product it is found in the hot springs of Lipari, and in those of Sasso in the Florentine territory. It is a constituent of several minerals, among which the datolite and boracite may in particular be mentioned. It occurs much more abundantly under the form of borax, a native compound of boracic acid and soda. It is prepared for chemical purposes by adding sulphuric acid to a solution of purified borax in about four times its weight of boiling water, till the liquid acquires a distinct acid reaction. The sulphuric acid unites with the soda; and the boracic acid is deposited, when the solution cools, in a confused group of shining scaly crystals. It is then thrown on a filter, washed with cold water to separate the adhering sulphate of soda and sulphuric acid, and still further purified by solution in boiling water and re-crystallization. But even after this treatment it is apt to retain a little sulphuric acid; on this account, when required to be absolutely pure, it should be fused in a platinum crucible, and once more dissolved in hot water and crystallized.

Prop.—In the crystallized state it is a hydrate, which contains 43·62 per cent. of water, being a ratio of 34·9 parts or 1 eq. of the anhydrous acid to 27 parts or 3 eq. of water. This hydrate dissolves in 25·7 times its weight of water at 60°, and in 3 times at 212°. Boiling alcohol dissolves it freely, and the solution, when set on fire, burns with a beautiful green flame; a test which affords the surest indication of the presence of boracic acid. Its sp. gr. is 1·479. It has no odour, and its taste is rather bitter than acid. It reddens litmus paper feebly, and effervesces with alkaline carbonates. Faraday has noticed that it renders turmeric paper brown like the alkalies. From the weakness of the acid properties of boracic acid, all the borates, when in solution, are decomposed by the stronger acids; and the neutral borates of potash and soda are deprived of half their base by carbonic acid, at common temperatures.

When hydrous boracic acid is exposed to a gradually increasing heat in a platinum crucible, its water of crystallization is wholly expelled, and a fused mass remains, which bears a white heat without being sublimed. On cooling it forms a hard, colourless, transparent glass, which is anhydrous boracic acid. If the water of crystallization be driven off by the sudden application of a strong heat, a large quantity of boracic acid is carried away during the rapid escape of watery vapour. The same happens, though in a less degree, when a solution of boracic acid in water is boiled briskly. But the loss of acid during the evaporation of its solution is sufficient to prevent its quantity from being accurately determined in this way; and in Tuscany the boracic acid which is collected in certain districts is brought up from below, along with aqueous vapour: this is conducted into cold water, in which the acid gradually accumulates, till it becomes worth while to evaporate the solution. Vitrified boracic acid should be preserved in well-stopped vessels; for if exposed to the air it absorbs water, and gradually loses its transparency. Its sp. gr. is 1·803. It is exceedingly fusible, and communicates this property to the substances with which it unites. For this reason borax is often used as a flux.

Its eq. is 34·9; symb. $B + 3O$, $\dddot{B}$, or BO_3.

SECTION X.

SILICON.

Hist.—That silicic acid or silica is composed of a combustible body united with oxygen, was demonstrated by Davy; for on bringing the vapour of potassium in contact with pure silicic acid heated to whiteness, a silicate of potassa resulted, through which was diffused the inflammable base of silicic acid in the form of black particles like plumbago. To this substance, on the supposition of its being a metal, the term *silicium* was applied. But though this view has been adopted by most chemists, so little was known with certainty concerning the real nature of the base of silicia, that Thomson inclined to the opinion of its being a non-metallic body, and accordingly associated it in his System of Chemistry with carbon and boron under the name of *silicon.* The recent researches of Berzelius appear almost decisive of this question. A substance which has not the metallic lustre, and is a non-conductor of electricity, cannot be regarded as a metal.

Prep.—Pure silicon was first procured by Berzelius in the year 1824 by the action of potassium on fluosilicic acid gas, but it is more conveniently prepared from the double fluoride of silicon and potassium or sodium, previously dried by a temperature near that of redness.

When this compound is heated in a glass tube with potassium, the latter unites with fluorine, and silicon is separated. The heat of a spirit-lamp is sufficient for the purpose, and the decomposition takes place, accompanied with feeble detonation, before the mixture becomes red-hot. When the mass is cold, the soluble parts are removed by the action of water; the first portions of which produce disengagement of hydrogen gas, owing to the presence of some silicuret of potassium. The silicon thus procured is chemically united with a little hydrogen, and at a red heat burns vividly in oxygen gas. In order to render it quite pure, it should be first heated to redness, and then digested in dilute hydrofluoric acid to dissolve adherent particles of silicic acid. (An. of Phil. xxvi. 116.)

Prop.—Silicon, obtained in this manner, has a dark nut-brown colour, without the least trace of metallic lustre. It is a non-conductor of electricity. It is incombustible in air and in oxygen gas; and may be exposed to the flame of the blow-pipe without fusing or undergoing any other change. It is neither dissolved nor oxidized by the sulphuric, nitric, hydrochloric, or hydrofluoric acids; but a mixture of the nitric and hydrofluoric acids dissolves it readily even in the cold.

It is not changed by ignition with chlorate of potassa. In nitre it does not deflagrate until the temperature is raised so high that the acid is decomposed; and then the oxidation is effected by the affinity of the disengaged alkali for silicic acid co-operating with the attraction of oxygen for silicon. For a similar reason it burns vividly when brought into contact with carbonate of potassa or soda, and the combustion ensues at a temperature considerably below that of redness. It explodes in consequence of a copious evolution of hydrogen gas, when it is dropped upon the fused hydrate of potassa, soda, or baryta.

Berzelius ascertained, by oxidizing a known weight of silicon, that 100 parts of silicic acid are composed of 48·4 of silicon and 51·6 of oxygen. Now, if silicic acid, as Thomson supposes, be composed of single atoms of its elements, then the equivalent of silicon will be 7·5; but if, as Berzelius believes, the smallest molecule of that acid contain 3 atoms of oxygen united with 1 atom of silicium, the equivalent of silicium would be 22·5. The latter view is supported by very strong analogies. Its equivalent is therefore 22·5; symb. Si.

Dr. S. Brown has endeavoured to show that silicon may be formed from carbon by isomeric transmutation. But his experiments were inconclusive, and have not been confirmed by those chemists who have repeated them. The subject of isomeric transmutation has been discussed in the section on Isomeric Bodies.

Silicic Acid.—Hist. and Prep.—This compound, known also by the names of *silica* and *siliceous earth*, exists abundantly in nature. It enters into the composition of most of the earthy minerals; and under the name of quartz rock, forms independent mountainous masses. It is the chief ingredient of sandstones, flint, calcedony, rock crystal, and other analogous substances. It may indeed be procured, of sufficient purity for most purposes, by igniting transparent specimens of rock crystal, throwing them while red-hot into water, and then reducing them to powder.

Prop.—Pure silicic acid, in this state, is a light white powder, which feels rough and dry when rubbed between the fingers; is both insipid and inodorous; the sp. gr. is 2·69. It is fixed in the fire, and very infusible; but fuses before the oxy-hydrogen blow-pipe with greater facility than lime or magnesia. It is quite insoluble in water; but Berzelius has shewn, that if presented to water while in the nascent state, it is dissolved in large quantity. On evaporating the solution gently, a bulky gelatinous hydrate separates, which is partially decomposed by a very moderate temperature, but does not part with all its water except at a red heat.

Silicic acid has no action on test paper; but in all its chemical relations it manifests the properties of an acid, and displaces carbonic acid from the alkalies by the aid of heat. Its combinations with the fixed alkalies are effected by mixing pure sand with carbonate of potassa or soda, and heating the mixture to redness. During the process, carbonic acid is expelled, and a silicate of the alkali is generated. The nature of the product depends upon the proportions which are employed. On igniting one part of silicic acid with three of carbonate of potassa, a vitreous mass is formed, which is deliquescent, and may be dissolved completely in water. This solution, which was formerly called *liquor silicum*, has an alkaline reaction, and absorbs carbonic acid on exposure to the atmosphere, by which it is partially decomposed. Concentrated acids precipitate the silicic acid as a gelatinous hydrate; but if a considerable quantity of water is present, and the acid is added gradually, the alkali may be perfectly neutralized without any separation of silicic acid. When a solution of this kind is evaporated to dryness, the silicic acid is rendered quite insoluble, and may thus be obtained in a pure form.

But if the proportion of silicic acid and alkali be reversed, a transparent brittle compound results, which is insoluble in water, is attacked by none of the acids excepting the hydrofluoric, and possesses the well known properties of glass. Every kind of ordinary glass is a silicate, and all its varieties are owing to differences in the proportion of the constituents, to the nature of the alkali, or to the presence of foreign matters. Thus, green bottle glass is made of impure materials, such as river sand, which contains iron, and the most common kind of kelp or pearl-ashes. Crown glass for windows is made of a purer alkali, and sand which is free from iron. Plate glass, for looking-glasses, is composed of sand and alkali in their purest state; and in the formation of flint-glass, besides these pure ingredients, a considerable quantity of litharge or red lead is employed. A small portion of peroxide of manganese is also used, in order to oxidize carbonaceous matters contained in the materials of the glass; and nitre is sometimes added with the same intention. Ordinary flint-glass, according to Faraday, contains 51·93 per cent. of silicic acid, 33·28 of oxide of lead, and 13·77 of potassa; proportions which correspond to 1 eq. of potassa, 1 eq. of oxide of lead, and nearly 4 eq. of silicic acid. Flint-glass, accordingly, is a double salt, consisting chiefly of bisilicate of potassa and bisilicate of oxide of lead.

Its eq. is 46·5; symb. $Si + 3O$, $\dddot{Si}$, or SiO_3.

SECTION XI.

SELENIUM.

Hist. and Prep.—This substance was discovered in 1818 by Berzelius, who called it selenium, from Σελήνη *the Moon*, a name suggested by its having at first been mistaken for the metal tellurium. (An. de Ch. et Ph. ix. 160, and An. of Phil. xiii. 401.) It has hitherto been obtained in very small quantity, and occurs for the most part in combination with some varieties of iron pyrites. Stromeyer has also detected it, as a sulphuret of selenium, among the volcanic products of the Lipari Isles. It is found likewise at Clausthal in the Hartz, combined, according to Stromeyer and Rose, with several metals, such as lead, cobalt, silver, mercury, and copper. Berzelius found it in the sulphur obtained by sublimation from the iron pyrites of Fahlun. In a manufactory of sulphuric acid, at which this sulphur was employed, it was observed that a reddish-coloured matter always collected at the bottom of the leaden chamber; and on burning this substance, Berzelius perceived a strong and peculiar odour, similar to that of decayed horse-radish, which induced him to submit it to a careful examination, and thus led to the discovery of selenium. For the extraction of the selenium from the native sulphuret, Magnus proposes to mix it with eight times its weight of peroxide of manganese, and to expose the mixture to a low red heat in a glass retort, the beak of which dips into water. The sulphur, oxidized at the expense of the manganese, escapes in the form of sulphurous acid; while the selenium either sublimes as such or in the state of selenious acid. Should any of the latter be carried over into the water, it would there be reduced by the sulphurous acid.

Prop.—Selenium, at common temperatures, is a brittle opaque solid body, without taste or odour. It has a metallic lustre and the aspect of lead, when in mass; but it is of a deep red colour when reduced to powder. Its sp. gr. is between 4·3 and 4·32. At 212° it softens, and is then so tenacious, that it may be drawn out into fine threads, which are transparent, and appear red by transmitted light. It becomes quite fluid at a temperature somewhat above that of boiling water. It boils at about 650°, forming a vapour which has a deep yellow colour, but is free from odour. It may be sublimed in close vessels without change, and condenses again into dark globules of a metallic lustre, or as a cinnabar-red powder, according as the space in which it collects is small or large. Berzelius at first regarded it as a metal; but since it is an imperfect conductor of heat and electricity, it more properly belongs to the class of the simple non-metallic bodies.

Selenium is insoluble in water. It suffers no change from mere exposure to the atmosphere; but if heated in the open air, it combines readily with oxygen, and two compounds, oxide of selenium and selenious acid, are generated. If exposed to the oxidizing part of the blow-pipe flame, it tinges the flame with a light blue colour, and exhales so strong an odour of decayed horse-radish, that 1-50th of a grain is said to be sufficient to scent the air of a large apartment. By this character the presence of selenium, whether alone or in combination, may always be detected.

Berzelius has shewn that selenic acid is composed of 24 parts of oxygen and 39·6 of selenium. This substance has three grades of oxidation, the oxygen in the last two of which is in the ratio of 2 and 3; and the highest grade, selenic acid, has in all its chemical relations a singularly close analogy to sulphuric acid. From these facts it is inferred that selenic acid is composed of 1 atom of selenium and 3 atoms of oxygen. The eq. of selenium is 39·6; symb. Se.

The compounds of selenium described in this section are the following:—

	Selenium.	Oxygen	Equiv.	Formulæ.
Oxide of Selenium (probably)	39·6 or 1 eq.	+ 8 or 1 eq.	= 47·6	SeO
Selenious Acid	39·6	+ 16 or 2 eq.	= 55·6	SeO_2
Selenic Acid	39·6	+ 24 or 3 eq.	= 63·6	SeO_3

Oxide of Selenium.—This compound is formed in greatest abundance by heating selenium in a limited quantity of atmospheric air, and by washing the product to separate selenious acid, which is generated at the same time. It is a colourless gas, which is very sparingly soluble in water, and does not possess any acid properties. It is the cause of the peculiar odour which is emitted during the oxidation of selenium.

Selenious Acid.—This acid is most conveniently prepared by digesting selenium in nitric or nitro-hydrochloric acid till it is completely dissolved. On evaporating the solution to dryness, a white residue is left, which is selenious acid. By increase of temperature, the acid itself sublimes, and condenses again unchanged into long four-sided needles. It attracts moisture from the air, whereby it suffers imperfect liquefaction. It dissolves in alcohol and water. It has distinct acid properties, and its salts are called *selenites.*

Selenious acid is readily decomposed by all substances which have a strong affinity for oxygen, such as sulphurous and phosphorous acids. When sulphurous acid, or an alkaline sulphite, is added to a solution of selenious acid, a red-coloured powder, pure selenium, is thrown down, and the sulphurous is converted into sulphuric acid. Hydrosulphuric acid also decomposes it; and an orange-yellow precipitate subsides, which is a sulphuret of selenium.

Selenic Acid.—Hist.—The preceding compound, discovered by Berzelius, was for some time the only known acid of selenium, and has been described in elementary works under the name of selenic acid; but the discovery of another acid of selenium, containing more oxygen than the other, has rendered necessary a change of nomenclature. The existence of selenic acid was first noticed by M. Nitzch, assistant to Mitscherlich, and its properties have been examined and described by the Professor himself. (Edin. Journal of Science, viii. 294.)

Prep.—This acid is prepared by fusing nitrate of potassa or soda with selenium, a metallic seleniuret, or with selenious acid or any of its salts. Seleniuret of lead, as the most common ore of selenium, will generally be employed; but it is very difficult to obtain pure selenic acid by its means, because it is commonly associated with metallic sulphurets. The ore is first treated with hydrochloric acid to remove any carbonate that may be present; and the insoluble part, which is about a third of the mass, is mixed with its own weight of nitrate of soda, and thrown by successive portions into a red-hot crucible. The lead is thus oxidized, and the selenium converted into selenic acid, which unites with soda. The fused mass is then acted on by hot water, which dissolves only seleniate of soda, together with nitrate and nitrite of soda; while the insoluble matter, when well washed, is quite free from selenium. The solution is next made to boil briskly, when anhydrous seleniate of soda is deposited; while, on cooling, nitrate of soda crystallizes. On renewing the ebullition and subsequent cooling, fresh portions of seleniate and nitrate are procured; and these successive operations are repeated, until the former salt is entirely separated. This process is founded on the fact that seleniate of soda, like the sulphate of the same base, is more soluble in water of about 90° than at higher or lower temperatures. The nitrite of soda, formed during the fusion, is purposely reconverted into nitrate by digestion with nitric acid.

The seleniate of soda thus procured always contains a little sulphuric acid, derived from the metallic sulphurets of the ore; and it is not possible to separate this acid by crystallization. All attempts to separate it by means of baryta were likewise fruitless; and the only method of effecting this object is by reducing the selenic acid into selenium. This is done by heating a mixture of seleniate of soda with hydrochlorate of ammonia, when the sodium unites with chlorine, all the hydrogen with oxygen, and selenium and nitrogen are set free. This change will be more readily followed when stated in symbols: thus,

$$\mathrm{NaO,SeO_3}, \text{ and } \mathrm{NH_3HCl}, \text{ yield } \mathrm{N,Se,4HO} \text{ and } \mathrm{NaCl}.$$

The selenium which sublimes is quite free from sulphur. It is then converted by nitric acid into selenious acid, which should be neutralized with soda, and fused with nitre or nitrate of soda. The pure seleniate of soda, separated from the nitrate according to the foregoing process, is subsequently dissolved in water, and obtained in crystals by spontaneous evaporation.

To procure the acid in a free state, seleniate of soda is decomposed by nitrate of oxide of lead. The seleniate of that oxide, which is as insoluble as the sulphate, after being well washed, is exposed to a current of hydrosulphuric acid gas, which precipitates all the lead as a sulphuret, but does not decompose the selenic acid. The excess of the gas is driven off by heat, and pure selenic acid remains diluted with water. The absence of fixed substances may be proved by its being volatilized by heat without residue; and, if free from sulphuric acid, it gives no precipitate with chloride of barium after being boiled with hydrochloric acid. Any nitric acid which may be present is expelled by concentrating the solution by means of heat.

Prop.—It is a colourless liquid, which may be heated to 536° with- appreciable decomposition; but above that point decomposition commences, and it becomes rapid at 554°, giving rise to disengagement of oxygen and selenious acid. When concentrated by a temperature of 329°, its sp. gr. is 2·524; at 512° it is 2·60, and at 545° it is 2·625, but a little selenious acid is then present. When procured by the process above described, selenic acid always contains water, but it is very difficult to ascertain its precise proportion. Some acid, which had been heated higher than 536°, contained, subtracting the quantity of selenious acid present, 15·75 per cent. of water, which approximates to the ratio of one equivalent of water and one of the acid. It is certain that selenic acid is decomposed by heat before parting with all the water which it contains.

Selenic acid has a powerful affinity for water, and emits as much heat in uniting with it as sulphuric acid does. Like this acid it is not decomposed by hydrosulphuric acid; and, hence, this gas may be employed for decomposing seleniate of the oxides of lead or copper. With hydrochloric acid the change is peculiar; for, on boiling the mixture, mutual decomposition ensues, water and selenious acid are formed, and chlorine is set free; so that the solution, like *aqua regia*, is capable of dissolving gold and platinum. Selenic acid dissolves zinc and iron with disengagement of hydrogen gas, and copper with formation of selenious acid. It dissolves gold also, but not platinum. Sulphurous acid has no action on selenic acid, whereas selenious acid is easily reduced by it. Consequently, when it is wished to precipitate selenium from selenic acid, it must be boiled with hydrochloric acid before sulphurous acid is added.

Mitscherlich has observed that selenic and sulphuric acids are not only analogous in composition and in many of their properties, but that the similarity runs through their compounds with alkaline substances, their salts resembling each other in chemical properties, constitution, and form.

SECTION XII.

CHLORINE.

Hist.—The discovery of chlorine was made in the year 1774 by Scheele, while investigating the nature of manganese, and he described it under the name of *dephlogisticated marine acid*. The French chemists called it *oxygenized muriatic acid*, a term which was afterwards contracted to *oxy-muriatic acid*, from an opinion proposed by Berthollet that it is a compound of *muriatic acid* and *oxygen*. In 1809 Gay-Lussac and Thenard published an abstract of some experiments upon this substance, which subsequently appeared at length in their Recherches Physico-Chimiques, wherein they stated that oxymuriatic acid might be regarded as a simple body, though they gave the preference to the doctrine advanced by Berthollet. Davy engaged in the inquiry about the same time; and after having exposed oxy-muriatic acid to the most powerful decomposing agents which chemists possess, without being able to effect its decomposition, he communicated to the Royal Society an essay, in which he denied its compound nature; and he maintained that, according to the true logic of chemistry, it is entitled to rank with simple bodies. This view, which is commonly termed the *new theory of chlorine*, though strongly objected to at the time it was first proposed, is now universally received by chemists. The grounds of preference will hereafter be briefly stated.

Prep.—Chlorine gas is obtained by the action of hydrochloric acid on peroxide of manganese. The most convenient method of preparing it is by mixing moderately strong hydrochloric acid, contained in a glass flask, with half its weight of finely-powdered peroxide of manganese. Effervescence, owing to the escape of chlorine, takes place even in the cold; but the gas is evolved much more freely by the application of a moderate heat. It should be collected by displacement of air in dry bottles. The tube conducting the gas reaches to the bottom of the bottle, where the chlorine, being heavier than air, accumulates, and displaces it. When the bottle is full, which is known by the colour of the gas appearing at the mouth of the bottle, it is stopped with a greased stopper, and another bottle put in its place. As some hydrochloric acid gas commonly passes over with it, the chlorine should be considered not quite pure till after being transmitted through water.

The theory of this process will be readily understood by first viewing the elements which act on each other; namely,

Manganese .	27·7 or 1 eq.	Mn	Chlorine .	70·84 or 2 eq.	2Cl
Oxygen .	16·0 or 2 eq.	2O	Hydrogen .	2·00 or 2 eq.	2H
Perox. of Mang.	43·7 or 1 eq.	Mn + 2O	Hydrochl. Acid	72.84 or 2 eq.	2(H+Cl);

and then inspecting the products derived from them, namely,

Manganese . .	27·7	Hydrogen .	2	Chlorine 35·42 or 1 eq.
Chlorine . .	35·42	Oxygen .	16	
Chlorine of Mang. .	63·12	Water .	18.	

In symbols,

MnO_2 and 2HCl yield MnCl,2HO, and Cl.

The affinities which determine these changes are the mutual attraction of oxygen and hydrogen, and of chlorine and manganese.

When it is an object to prepare chlorine at the cheapest rate, as for the purposes of manufacture, the preceding process is modified in the following manner:—Three parts of sea-salt are intimately mixed with one of peroxide of manganese, and to this mixture two parts of sulphuric acid, diluted with an equal weight of water, are added. By the action of sulphuric acid on sea-salt, hydrochloric acid is disengaged, which reacts, as in the former case, upon the peroxide of manganese; so that, instead of adding hydrochloric acid directly to the manganese, the materials for forming it are employed. In this process, however, the sulphates of soda and protoxide of manganese are generated, instead of chloride of manganese. Thus, the materials which act on each other are MnO_2, $NaCl$, and $2SO_3$; and the products MnO,SO_3; NaO,SO_3; and Cl.

Prop.—Chlorine (from *χλωρος green*) is a yellowish-green coloured gas, which has an astringent taste and a disagreeable odour. It is one of the most suffocating of the gases, exciting spasm and great irritation of the glottis, even when considerably diluted with air. When strongly and suddenly compressed, it emits both heat and light, the latter being solely due, as in the case of air and oxygen, to the chlorine acting chemically on the oil with which the compressing apparatus is lubricated. (An. de Ch. et Ph. xliv. 181.) According to Davy, 100 cubic inches of dry chlorine at 30° B. and 60° F. weigh between 76 and 77 grains. Gay-Lussac and Thenard found the density of pure and dry chlorine to be 2·47, which gives 76·599 grains as the weight of 100 cubic inches at 60° F. and 30° B. Under the pressure of about four atmospheres it is a limpid liquid of a bright yellow colour, which does not freeze at the temperature of zero, and which assumes the gaseous form with the appearance of ebullition when the pressure is removed. Kemp finds that this liquid is a non-conductor of electricity.

Cold recently boiled water, at the common pressure, absorbs twice its volume of chlorine, and yields it again when heated. The solution, which is made by transmitting a current of chlorine gas through cold water, has the colour, taste, and most of the other properties of the gas itself. When moist chlorine gas is exposed to a cold of 32°, yellow crystals are formed, which consist of water and chlorine in definite proportions. They are composed, according to Faraday, of 35·42 parts or 1 eq. of chlorine, and 90 parts or 10 eq. of water. It experiences no chemical change from the action of the imponderables. Thus it is not affected chemically by intense heat, by strong shocks of electricity, or by a powerful galvanic battery. Davy exposed it also to the action of charcoal heated to whiteness by galvanic electricity, without separating oxygen from it, or in any way affecting its nature. Light does not act on dry chlorine; but if water be present, the chlorine decomposes that liquid, unites with the hydrogen to form hydrochloric acid, and oxygen gas is set at liberty. This change takes place quickly in sunshine, more slowly in diffused daylight, and not at all when light is wholly excluded. Hence the necessity of keeping moist chlorine gas, or its solution, in a dark place.

Chlorine unites with some substances with evolution of heat and light, and is hence termed a supporter of combustion. On plunging a lighted taper into chlorine gas, it burns for a short time with a small red flame, and emits a large quantity of smoke. Phosphorus takes fire in it spontaneously, and burns with a pale white light. Several of the metals, such as tin, copper, arsenic, antimony, and zinc, when introduced into chlorine in the state of powder or in fine leaves, are suddenly inflamed. In all these cases the combustible substances unite with chlorine.

Chlorine has a very powerful attraction for hydrogen; and many of the chemical phenomena to which it gives rise are owing to this property. A striking example is its power of decomposing water by the action of light, or at a red heat: the same effect is produced on most compound substances of which hydrogen is an element. For the same reason, when chlorine, water, and some other body which has a strong affinity for oxygen, are presented to one another, water is usually resolved into its elements, its hydrogen attaching itself to the chlorine, and its oxygen to the other body. Thus chlorine is, indirectly, one of the most powerful oxidizing agents which we possess.

When any compound of chlorine and an inflammable body is exposed to the influence of galvanism, the inflammable body goes over to the —, and chlorine to the + pole of the battery. This establishes a close analogy between oxygen and chlorine, both of them being supporters of combustion, and both negative electrics.

Though formerly called an acid, it possesses no acid properties. It has not a sour taste, does not redden the blue colour of plants, and shows comparatively little disposition to unite with alkalies. Its strong affinity for the metals is sufficient to prove that it is not an acid; for chemists are not acquainted with any instance of an acid combining directly in definite proportion with a metal. Its action on the pure alkalies leads to complicated changes, which will be considered while speaking of the oxides of chlorine.

One of the most important properties of chlorine is its bleaching power. All animal and vegetable colours are speedily removed by chlorine; and when the colour is once discharged, it can never be restored. Davy proved that chlorine cannot bleach unless water is present. Thus dry litmus paper suffers no change in dry chlorine; but when water is admitted, the colour speedily disappears. It is well known also that hydrochloric acid is always generated when chlorine bleaches. From these facts it is inferred that water is decomposed during the process; that its hydrogen unites with chlorine, and that decomposition of the colouring matter is occasioned by the oxygen which is liberated. The bleaching property of binoxide of hydrogen and of chromic and permanganic acids, of which oxygen is certainly the decolorizing principle, leaves little doubt of the accuracy of the foregoing explanation.

Chlorine is useful, likewise, for the purposes of fumigation. The experience of Guyton-Morveau is sufficient evidence of its power in destroying the volatile principles given off by putrefying animal matter; it probably acts in a similar way on contagious effluvia. A peculiar compound, formed by the action of chlorine on soda, has been lately introduced for this purpose by Labarraque.

Chlorine is in general easily recognized by its colour and odour. Chemically it may be detected by its bleaching property, added to the circumstance that a solution of nitrate of oxide of silver occasions in it a dense white precipitate (a compound of chlorine and metallic silver), which becomes dark on exposure to light, is insoluble in acids, and dissolves completely in pure ammonia. The whole of the chlorine, however, is not thrown down; for the oxygen of the oxide of silver unites with a portion of chlorine, and converts it into chloric acid.

Those compounds of chlorine, which are not acid, are termed *chlorides* or *chlorurets.* The former expression, from the analogy between chlorine and oxygen, is perhaps the more appropriate.

Berzelius inferred the equivalent of chlorine from the oxygen lost by chlorate of potassa when decomposed by heat, and the quantity of chlorine found in the residual chloride of potassium. I investigated the same subject by examining into the composition of the nitrate of the oxide of silver, and the chloride of silver, of the protoxide and chloride of lead, and of the peroxide and chlorides of mercury. These researches concur in showing 36, the eq. of chlorine commonly adopted in this country, to be erroneous. The number inferred from the sp. gr. of chlorine and hydrogen gases is 35·84; but, unfortunately, the densities of these gases are not known with the precision required for an application of this nature.

Its eq. is 35·42; eq. vol. = 100; symb. Cl.

The composition of the compounds described in this section is as follows:—

	Chlorine.					Equiv.	Formulæ.
Hydrochloric Acid	35·42	1 eq.	+ Hydrogen	1	1 eq. =	36·42	HCl.
Hypochlorous Acid	35·42		+ Oxygen	8	1 eq. =	43·42	ClO.
Chlorous Acid of Millon .	35·42		+ Ditto	24	3 eq. =	59·42	ClO_3.
Chlorous Acid .	35·42		+ Ditto	32	4 eq. =	67·42	ClO_4.
Chloric Acid .	35·42		+ Ditto	40	5 eq. =	75·42	ClO_5.
Perchloric Acid .	35·42		+ Ditto	56	7 eq. =	91·42	ClO_7.

	Chlorine.				Equiv.	Formulæ.
Chlorochloric Acid	107·26	3 eq. + Ditto	104	13 eq. =	211·26	Cl_3O_{13}.
Chloroperchloric Acid	107·26	3 eq. + Ditto	128	17 eq. =	235·26	Cl_3O_{17}.
Quadrochloride of Nitrogen	141·68	4 eq. + Nitrogen	14·15	1 eq. =	155·83	NCl_4.
Protochloride of Carbon	35·42	1 eq. + Carbon	6·12	1 eq. =	41·54	CCl.
Dichloride of Carbon	35·42	1 eq. + Ditto	12·24	2 eq. =	47·66	C_2Cl.
Perchloride of Carbon	106·26	3 eq. + Ditto	12·24	2 eq. =	118·5	C_2Cl_3.
Dichloride of Sulphur	35·42	1 eq. + Sulphur	32·2	2 eq. =	67·62	SCl.
Protochloride of Sulphur	35·42	1 eq. + Ditto	16·1	1 eq. =	51·52	SCl.
Sesquichloride of Phosphorus	106·26	3 eq. + Phospho.	31·4	1 eq. =	137·66	P_2Cl_3.
Perchloride of Phosphorus	175	5 eq. + Ditto	31·4	1 eq. =	206·4	P_2Cl_5.
Chlorocarbonic Acid Gas	35·42	1 eq. + Carb. ox.	14·12	1 eq. =	49·54	CO+Cl.
Terchloride of Boron	106·26	3 eq. + Boron	10·9	1 eq. =	117·16	BCl_3.
Terchloride of Silicon	106·26	3 eq. + Silicon	22·5	1 eq. =	128·76	$SiCl_3$.

Hydrochloric Acid.—Hist. and Prep.—A concentrated aqueous solution of this acid has been long known under the names of spirit of salt, and of marine or muriatic acid; but in its purer form of gas it was discovered in 1772 by Priestley. It may be conveniently prepared by putting an ounce of strong hydrochloric acid solution into a glass flask, and heating it by means of a lamp till the liquid boils, when the gas is freely evolved, and may be collected over mercury. Another method of preparing it is by the action of sulphuric acid of sp. gr. 1·750 on an equal weight of sea-salt. Brisk effervescence ensues at the moment of making the mixture, and on the application of heat a large quantity of hydrochloric acid gas is disengaged. In the former process, hydrochloric acid previously dissolved in water is simply expelled from the solution by heat. The explanation of the latter process is more complicated. Sea-salt was formerly supposed to be a compound of hydrochloric acid and soda; and, on this supposition, the soda was believed merely to quit the hydrochloric and unite with sulphuric acid. But the researches of Gay-Lussac, Thenard, and Davy proved that it consists of chlorine and sodium combined in the ratio of their equivalents. The nature of its action with sulphuric acid will be understood by comparing the elements concerned in the change before and after it has occurred.

Hydrous Sulp. Acid.			Chloride of Sodium.		Sulph. of Soda.			Hydrochloric Acid.	
Real Acid		40·1	Chlorine	35·42	Acid		40·1	Chlorine	35·42
Water	Hyd.	1	Sodium	23·3	Soda	Sod.	23·3	Hydrogen	1
	Oxy.	8				Oxy.	8		

or in symbols,

$$HO,SO_3 + NaCl = NaO,SO_3 + HCl.$$

Thus it appears that single equivalents of water, sulphuric acid, and chloride of sodium yield sulphate of soda and hydrochloric acid. The water of the sulphuric acid is essential; so much so, indeed, that chloride of sodium is not decomposed at all by anhydrous sulphuric acid.

Hydrochloric acid may be generated by the direct union of its elements. When equal measures of chlorine and hydrogen are mixed together, and an electric spark is passed through the mixture, instantaneous combination takes place, heat and light are emitted, and hydrochloric acid is generated. A similar effect is produced by flame, by a red-hot body, and by spongy platinum. Light also causes them to unite. A mixture of the two gases may be preserved without change in a dark place; but if exposed to the diffused light of day, gradual combination ensues, which is completed in the course of 24 hours. The direct solar rays produce, like flame and electricity, sudden inflammation of the whole mixture, accompanied with explosion; and, according to Brande, the vivid light emitted by charcoal intensely heated by galvanic electricity acts in a similar manner.

Prop.—It is a colourless gas, has a pungent odour and an acid taste. Under a pressure of 40 atmospheres, and at the temperature of 50°, it is liquid. Sp. gr. 1·2695. It is quite irrespirable, exciting violent spasm of the glottis; but, when diluted with air, it is far less irritating than chlorine. All burning bodies are extinguished by it, nor is the gas itself inflammable.

It is not chemically changed by mere heat. It is readily decomposed by galvanism, hydrogen appearing at the —, and chlorine at the + pole. It is also decomposed by ordinary electricity. The decomposition, however, is incomplete; for, though one electric spark resolves a portion of the gas into its elements, the next shock in a great measure effects their reunion. It is not effected by oxygen under common circumstances; but if a mixture of oxygen and hydrochloric acid gases is electrified, the oxygen unites with the hydrogen of the acid to form water, and chlorine is set at liberty. For this and the preceding fact we are indebted to the researches of Henry.

One of the most striking properties of hydrochloric acid gas is its powerful attraction for water. A dense white cloud appears whenever it escapes into the air, owing to its combining with the aqueous vapour of the atmosphere. A piece of ice put into a jar full of the gas confined over mercury liquefies on the instant, and the whole of the gas disappears in the course of a few seconds. On opening a long wide jar of hydrochloric acid gas under water, the absorption of the gas takes place so instantaneously, that the water is forced up into the jar with the same violence as into a vacuum. Considerable increase of temperature takes place during the absorption, and therefore the apparatus should be kept cool by ice. Davy states (Elements, p. 252) that water at the temperature of 40° absorbs 480 times its volume of the gas, and that the solution has a sp. gr. of 1·2109. Thomson finds that one cubic inch of water at 69° absorbs 418 cubic inches of gas, and occupies the space of 1·34 cubic inch. The solution has a sp. gr. of 1·1958, and one cubic inch of it contains 311·04 cubic inches of hydrochloric acid gas. The quantity of real acid contained in solutions of different densities may be determined by ascertaining the quantity of pure marble dissolved by a given weight of each. Every 50·6 grains of marble correspond to 36·42 of real acid. The following table, from Thomson's Principles of Chemistry, is constructed according to this rule. The first and second columns show the atomic constitution of each acid.

Table exhibiting the Specific Gravity of Muriatic Acid of determinate Strengths.

Atoms of Acid.	Atoms of Water.	Real Acid in 100 of the Liquid.	Specific Gravity.	Atoms of Acid.	Atoms of Water.	Real Acid in 100 of the Liquid.	Specific Gravity.
1	6	40·659	1·2030	1	14	22·700	1·1060
1	7	37·000	1·1790	1	15	21·512	1·1008
1	8	33·945	1·1620	1	16	20·442	1·0960
1	9	31·346	1·1490	1	17	19·474	1·0902
1	10	29·134	1·1390	1	18	18·590	1·0860
1	11	27·206	1·1285	1	19	17·790	1·0820
1	12	25·517	1·1197	1	20	17·051	1·0780
1	13	24·026	1·1127				

The different pharmacopœias give processes for preparing the aqueous solution of this acid, but the following process, proposed by Gregory, is now universally followed. Six parts, by weight, of pure salt are introduced into a flask or balloon, in which is first placed a mixture of 10 parts, by weight, of oil of vitriol, and 4 parts of water, previously allowed to cool. A long tube twice bent at right angles, with a bulb on the descending limb, is now tightly fitted to the flask by means of a cork, and the point of the tube is made just to touch the surface of a quantity of distilled water equal in weight to the salt, and placed in a bottle surrounded with ice or ice-cold water. A gentle heat is now applied to the flask, which rests in a sand-pot, and continued as long as any gas passes over. Two-thirds of the hydrochloric acid pass over quite dry, but the last third is accompanied by watery vapour, which is known by the further end of the tube becoming heated. As soon as this is observed, the water in the bottle may be removed and replaced by half the quantity of distilled water, which yields a portion of acid not so strong as the first. The water first charged has now a sp. gr. of 1·14, and the second portion has the sp.

gr. 1·10 or thereabouts. Both portions are perfectly pure, if the materials have been so, for no sulphuric acid reaches even the tube, in consequence of the previous dilution of the oil of vitriol, which enables the decomposition to take place at so low a temperature that no sulphuric acid is volatilized. This addition of water has another good effect: it causes the residue of bisulphate of soda to assume the form of a soft semifluid mass easily removed from the vessel, while the residue, when oil of vitriol is used undiluted, is so hard and so difficult to dissolve, as to cause in a majority of cases the loss of the flask.

The acid, as above prepared, is strong and fuming, and ought to be quite colourless, which is never the case with the hydrochloric acid of commerce, in which chloride of iron and free chlorine both contribute to produce a yellow colour.

If it be desired to obtain hydrochloric acid of the highest degree of concentration, when it has a sp. gr. of 1·21, this is easily done by charging the flask anew, and causing the first two-thirds of the gas given off to pass through any convenient quantity of the acid first prepared, surrounded by ice-cold water, until it refuses to absorb any more.

In the whole of this process no safety-tube is required, since, if the tube touch the water, no gas whatever will escape until the water is saturated with it, unless we neglect to keep it cool, in which case the heat always given out when a gas is rapidly absorbed raises the temperature so much as to prevent further absorption. The tube is to be kept near the surface of the water, that is, just dipping into it, because the water, by combining with the gas, becomes heavier, sinks, and is replaced by lighter fluid, which in its turn becomes heavier and sinks, and thus a perfect mixture is obtained. As the water, in proportion as it absorbs the gas, increases in bulk, the vessel containing it must be from time to time lowered, so that the tube may continue just to dip under the surface.

The concentrated solution of pure hydrochloric acid is a colourless liquid, which emits white vapours when exposed to the air, is intensely sour, reddens litmus paper strongly, and neutralizes alkalies. It combines with water in every proportion, and causes increase of temperature when mixed with it, though in a much less degree than sulphuric acid. It freezes at − 60° F.; and boils at 110°, or a little higher, giving off pure hydrochloric acid gas in large quantity.

The hydrochloric acid of commerce has a yellow colour, and is always impure. Its usual impurities are free chlorine, sulphuric acid, and chloride of iron. The presence of free chlorine may be inferred if the hydrochloric acid has the property of dissolving gold leaf. Iron may be detected by ferrocyanuret of potassium, and sulphuric acid by chloride of barium, the suspected hydrochloric acid being previously diluted with three or four parts of water.

Hydrochloric acid is decomposed by substances which yield oxygen readily. Thus several peroxides, such as those of manganese, cobalt, and lead, effect its decomposition. Chloric, iodic, bromic, nitric, and selenic acids act on the same principle. A mixture of nitric and hydrochloric acids, in the ratio of one measure of the former to two of the latter, has long been known under the name of *Aqua regia*, as a solvent for gold and platinum. When these acids are mixed together, the solution instantly becomes yellow; and on heating the mixture, pure chlorine is evolved, and the colour of the solution deepens. On continuing the heat, chlorine and nitrous acid vapours are disengaged. At length the evolution of chlorine ceases, and the residual liquor is found to be a solution of hydrochloric and nitrous acids, which is incapable of dissolving gold. The explanation of these facts is, that nitric and hydrochloric acids decompose one another, giving rise to the production of water and nitrous acid, and the separation of chlorine; while hydrochloric and nitrous acids may be heated together without mutual decomposition. It is hence inferred that the power of nitro-hydrochloric acid in dissolving gold is owing to the chlorine which is liberated. (Davy, in the Quarterly Journal, vol. i.) Baudrimont states that when a mixture of 2 parts of nitric acid and 3 of hydrochloric acid is heated to 187°, a red gas is given off, which, if passed through well-cooled tubes, condenses into a red liquid. It is soluble in water, forming a red solution, which has all the properties of aqua regia. According to Baudrimont, the composition of this compound, which he calls chloronitric acid, is NO_3,Cl_2 and it may be viewed as nitric acid, in which 2 eq. of oxygen are replaced by chlorine. (Jour. de Phar. v. 49.) Koene (Kong. Vet. Akad. Handl. 1844) denies the existence of this compound.

Hydrochloric acid is distinguished by its odour, volatility, and strong acid properties. With nitrate of oxide of silver it yields the same precipitate as chlorine; but no chloric acid is generated, because the oxygen of the oxide of silver unites with the hydrogen of the hydrochloric acid, and the chlorine in consequence is entirely precipitated. Notwithstanding that nitrate of oxide of silver yields the same precipitate with chlorine and hydrochloric acid, there is no difficulty in distinguishing between them; for the bleaching property of the former is a sure ground of distinction.

The composition of hydrochloric acid has been determined by Davy, and Gay-Lussac and Thenard. Their experiments concur in proving that chlorine and hydrogen unite in equal volumes, and that the hydrochloric acid, which is the sole and constant product, occupies the same space as the gases from which it is formed. From these facts the composition of hydrochloric acid is easily inferred. For, as

	Grains.
50 cubic inches of Chlorine weigh	38·2990
50 „ „ of Hydrogen	1·0699
100 C. I of Hydrochloric Acid Gas must weigh . . .	39·3689

These numbers are in the ratio of 1 to 35·84, being nearly that of a single eq. of hydrogen and chlorine. Hence its eq. is 36·42; eq. vol. $=100$; symb. $H + Cl$, or HCl.

COMPOUNDS OF CHLORINE AND OXYGEN.

The leading character of these compounds is derived from the circumstance that chlorine and oxygen, the attraction of which for most elementary substances is so energetic, have but a feeble affinity for each other. These principles, consequently, are never met with in nature in a state of combination. Indeed, they cannot be made to combine directly; and when they do unite, very slight causes effect their separation. Chemists have long been doubtful as to the exact number of the compounds of chlorine and oxygen. The recent labours of Balard, Martens, and Millon have established the existence of seven, all of which they have shewn to possess acid properties. Their names and constitutions are given in the subjoined table.

	By Weight.		By Volume.	
	Chl.	Oxy.	Chl.	Oxy.
Hypochlorous Acid . .	35·42	8	2	1
Chlorous Acid of Millon .	35·42	8	2	3
Chlorous Acid . . .	35·42	32	2	4
Chloric Acid . .	35·42	40	2	5
Perchloric Acid . . .	35·42	56	2	7
Chlorochloric Acid . .	107·26	104	6	13
Chloroperchloric Acid . .	107·26	128	6	17

According to the practice of most British chemists, two volumes of chlorine, as also two volumes of hydrogen and of nitrogen, are considered as respectively corresponding to one equivalent or one atom; whereas one volume of oxygen corresponds to one equivalent. Berzelius, with many Continental chemists, considering the atoms of all elements to possess the same volume, regard the first five of the above compounds as composed of 2 atoms or 2 eqs. of chlorine combined with 1, 3, 4, 5, or 7 atoms or eqs. of oxygen.

Hypochlorous Acid.—Hist. and Prep.—Davy, in 1811, discovered a gaseous compound, which was described by him in the Philosophical

Transactions of the same year, under the name of Euchlorine. This gas, which until recently has been considered to be the protoxide of chlorine, is made by the action of hydrochloric acid on the chlorate of potassa; and its production is explicable by the fact that hydrochloric and chloric acids mutually decompose each other. When hydrochloric acid and chlorate of potassa are mixed together, more or less of the potassa is separated by the hydrochloric from the chloric acid, and the latter being set at liberty, reacts on free hydrochloric acid. The result depends upon the relative quantities of the materials. If hydrochloric acid be in excess, the chloric acid undergoes complete decomposition. For each eq. of chloric acid, 5 eq. of hydrochloric acid are decomposed: the 5 eq. of oxygen, contained in the former, unite with the hydrogen of the latter, producing 5 eq. of water; while the chlorine of both acids is disengaged. If, on the contrary, chlorate of potassa be in excess, the chloric acid is deprived of part of its oxygen only; the products are water and the euchlorine of Davy. The chloric and hydrochloric acids react on each other in the ratio of 1 eq. to 2, or what is the same thing, in that of 4 eq. to 8 eq.: thus,

$$4ClO_5 + 8HCl = 8HO + 12ClO.$$

The gas thus obtained, though containing chlorine and oxygen in the ratio of atom to atom, is not, as was supposed by Davy, a distinct compound, but is a mixture of chlorine and chlorous acid. For this fact, which has long been suspected, we are indebted to the researches of Soubeiran. On transmitting a stream of euchlorine through a tube nearly full of calomel, the free chlorine is readily absorbed; on subsequently exploding the purified gas, he obtained one volume of chlorine to two volumes of oxygen, being the exact composition of chlorous acid. The product of the last decomposition is therefore

$$3ClO_4 + 9Cl, \text{ and not } 12ClO.$$

The experiments of Soubeiran have been confirmed by the discoveries of Balard.

If a stream of chlorine gas be passed into a solution of the pure alkalies, or be allowed to act upon the alkaline earths in the form of hydrates, a bleaching substance is procured, which has been commonly viewed as a direct compound of chlorine and an alkaline base. It consists, however, according to Balard, of a mixture of a metallic chloride and the hypochlorite of the alkali employed. (An. de Ch. et Ph. lvii. 225.) The process recommended for obtaining the pure acid is to pour into bottles filled with chlorine gas peroxide of mercury in fine powder, and mixed with twice its weight of distilled water: by brisk agitation the chlorine is rapidly and completely absorbed, if a slight excess of the peroxide be used. By this process one portion of the peroxide of mercury, HgO_2, is decomposed, both its constituents combining with chlorine, the mercury forming corrosive sublimate, $HgCl_2$, and the oxygen hypochlorous acid. The latter remains in solution in the water; while the former, by combining with undecomposed peroxide of mercury, forms the sparingly soluble oxychloride of mercury, which is separated by filtration. The hypochlorous acid being volatile, is obtained in a pure but diluted state by distillation. The temperature which is used for this purpose should be kept considerably below 212°, as the hypochlorous acid decomposes rapidly at that heat: the process is, therefore, best performed under reduced pressure. A more concentrated solution of the acid is obtained by submitting the first products to a second distillation.

Prop.—As thus obtained, hypochlorous acid is a transparent liquid of a slightly yellow colour when concentrated. Its odour is strong and penetrating, and distinct from, though somewhat similar to, that of chlorine. Its action on the skin is exceedingly powerful, the effect being even greater than that produced by nitric acid. It is a highly bleaching compound. In a concentrated state it is very unstable, a slow decomposition taking place at common temperatures, by which chlorine is evolved and chloric acid produced. This change is promoted by light, and is effected almost instantly by exposure for a few moments to the direct rays of the sun. It is also decomposed by agitation with angular bodies; and on throwing into the acid a portion of pounded glass, a brisk effervescence is observed from the escape of chlorine.

It is one of the most powerful oxidizing agents. Its action in this respect, however, is various, and is principally observed in relation to the simple non-metallic elements. Thus sulphur and phosphorus are readily brought to their highest state of oxidation, and even selenium is converted into selenic acid, an effect which the nitric acid cannot accomplish. Iodine and bromine are also instantly changed into iodic and bromic acids. Its action on the more perfect metals, on the contrary, is slight: iron and silver, however, are remarkable exceptions to this rule; for, when either of them is brought in a finely divided state in contact with hypochlorous acid, the latter suffers instantaneous decomposition. When iron is used, it is oxidized at the expense of the acid, and chlorine is evolved; with silver the oxygen escapes, and the chlorine unites exclusively with the metal. The decomposition of hypochlorous acid may also be produced by metallic mercury; but the decomposition is unattended by the evolution of either gas. Both the chloride and oxide of mercury are produced, and instantly unite to form, the oxychloride.

Balard has also succeeded in obtaining hypochlorous acid in the gaseous form. A small quantity of a concentrated solution is introduced into a bell jar over mercury, and fragments of dry nitrate of lime are successively added. The nitrate of lime being highly deliquescent, unites with the water, and the acid gas escapes with effervescence: the presence of the saline solution is essential, as it prevents the decomposition of the gas by the mercury. The gas is of a yellowish-green colour, and is very similar to chlorine in appearance. It unites rapidly by water, which absorbs at least 100 times its own volume of gas. It detonates by a slight increase of temperature; and, though less explosive than the chlorous acid, there is a probability of an accident in transferring it from one vessel to another. The results of explosion are oxygen and chlorine; and Balard found that 100 measures produced 100 of chlorine and 50 of oxygen. From these data its sp. gr. is 3·0212; its eq. 43·42; eq. vol. = 100; symb. $Cl + O$, $\dot{Cl}$, or ClO.

Chlorous Acid.—Hist. and Prep.—This compound was discovered by Davy in 1815 (Phil. Trans.), and soon after by Count Stadion of Vienna. It is formed by the action of sulphuric acid on chlorate of potassa. A quantity of this salt, not exceeding 50 or 60 grains, is reduced to powder, and made into a paste by the addition of some strong sulphuric acid. The mixture, which acquires a deep yellow colour, is placed in a glass retort, and heated by warm water, the temperature of which is kept under 212° F. A bright yellowish-green gas, of a richer colour than chlorine, is disengaged, which has an aromatic odour, without any smell of chlorine, is absorbed rapidly by water, to which it communicates its tint. This gas, which has long been described as the peroxide of chlorine, must now be called chlorous acid, as it has been shewn to possess acid properties, and to form definite compounds with the alkaline bases.

The chemical changes which take place in the process are explained in the following manner:—The sulphuric acid decomposes some of the chlorate of potassa, and sets chloric acid at liberty. The chloric acid, at the moment of separation, resolves itself into peroxide of chlorine and oxygen; the last of which, instead of escaping as free oxygen gas, goes over to the acid of some undecomposed chlorate of potassa, and converts it into perchloric acid. The products are bisulphate and perchlorate of potassa, and chlorous acid. It is most probable, from the data contained in the preceding table, that every 3 eq. of chloric acid yield 1 eq. of perchloric acid and 2 eq. of chlorous acid.

Prop.—Chlorous acid unites readily with the alkalies and alkaline earth, forming salts which are more stable than those of the hypochlorous acid. They are produced by transmitting the gas into the alkaline solutions, which may thus be rendered perfectly neutral. (Martens, An. de Ch. et Ph. lxi. 293.) All the salts hitherto examined are soluble in water, and are possessed, like the acid itself, of bleaching properties. The neutral salts pass readily into a metallic chloride and chlorate of the base, particularly such as the chloride of potash, which form a sparingly soluble chlorate. This change does not so readily ensue when alkali is in excess. The proportion in which the chloride and chlorate are produced indicate that 6 eq. of chlorite are decomposed, by which 1 eq. of metallic chloride and 5 eq. of chlorate are produced: thus, $6KO,ClO_4$ yields KCl and $5KO,ClO_5$. The solution of the pure acid gradually yields chloric acid and chlorine. It is a powerful oxidizing agent, and in this respect is very similar to the hypochlorous acid. It causes a precipitate with nitrate of silver; but it is best recognized by the evolution of chlorous acid gas on the addition of an acid to its salts.

Phosphorus takes fire when introduced into the gas, and occasions an explosion. It explodes violently when heated to a temperature of 212°, emits a strong light, and undergoes a greater expansion than protoxide of chlorine. According to Davy, whose result is confirmed by Gay-Lussac, 40 measures of the gas occupy after explosion the space of 60 measures; and of these, 20 are chlorine and 40 oxygen. The peroxide is therefore composed of 35·42 parts, or 1 eq. of chlorine, united with 32 or 4 eq. of oxygen; and its sp. gr. must be 23·375.

Its eq. is 67·42: eq. vol. = 100; symb. $Cl + 4O$, $\overset{\cdot\cdot\cdot\cdot}{\mathrm{Cl}}$, or ClO_4. Millon gives to this acid the name of hypochloric acid, and confines that of chlorous acid to a compound described by him, the composition of which he states to be ClO_3. Its properties resemble those of the two preceding acids.

Chloric Acid.—*Prep.*—If a current of chlorine gas be transmitted into a strong solution of pure potassa, a portion of the alkali is decomposed, and chloride of potassium and hypochlorate of potassa are generated, equivalent for equivalent. On bringing the solution to the boiling point, the latter salt is decomposed. The changes which occur are complicated, and give rise to the evolution of oxygen, and the formation of chlorate of potassa and chloride of potassium. According to the experiments of Morin and Soubeiran, which accord entirely with the observations of Balard, 9 eq. of hypochlorite of potassa produce 1 eq. of chlorate of potassa, 8 eq. of chloride of potassium, and 12 eq. of oxygen; or thus:

$$9(KO + ClO) \text{ yield } (KO + ClO_5), 8KCl, \text{ and } 12O.$$

Hence for every eq. of chlorate, 17 eq. of chloride are formed.

When to a dilute solution of chlorate of baryta a quantity of weak sulphuric acid, exactly sufficient for combining with the baryta, is added, the insoluble sulphate of baryta subsides, and pure chloric acid remains in the liquid. This acid, the existence of which was originally observed by Mr. Chenevix, was first obtained in a separate state by Gay-Lussac.

Prop.—Chloric acid reddens vegetable blue colours, has a sour taste, and forms neutral salts, called *chlorates* (formerly *hyperoxymuriates*), with alkaline bases. The best and most economical method of preparing chlorate of potassa will be given in the section on salts. It possesses no bleaching properties, a circumstance by which it is distinguished from chlorine, hypochlorous, and chlorous acids. It gives no precipitate in solution of nitrate of oxide of silver, and hence cannot be mistaken for hydrochloric acid. Its solution may be concentrated by gentle heat till it acquires an oily consistence without decomposition: in this state of highest concentration it acquires a yellowish tint, emits an odour of nitric acid, sets fire to paper and other dry organic matter, and converts alcohol into acetic acid. When sharply heated in a retort, part of the acid is resolved into chlorine and oxygen; but another portion, acquiring oxygen from that which is decomposed, is converted into perchloric acid, and then passes over into the receiver in the form of a dense colourless liquid (Serullas). Chloric acid is easily decomposed by deoxidizing agents. Sulphurous acid, for instance, deprives it of oxygen, with formation of sulphuric acid and evolution of chlorine. By the action of hydrosulphuric acid, water is generated, while sulphur and chlorine are set free. The power of hydrochloric acid in effecting its decomposition has already been explained.

Chloric acid is readily known by forming a salt with potassa, which crystallizes in tables and has a pearly lustre, deflagrates like nitre when flung on burning charcoal, and yields peroxide of chlorine by the action of concentrated sulphuric acid. Chlorate of potassa, like most of the chlorates, gives off pure oxygen when heated to redness, and leaves a residue of chloride of potassium. By this mode Gay-Lussac ascertained the composition of chloric acid, as stated in the preceding table. (An. de Chimie, xci.)

Its eq. is 75·42; symb, $Cl + 5O$, $\overset{\cdot\because\cdot}{Cl}$, or ClO_5.

Perchloric Acid.—The saline matter which remains in the retort after forming chlorous acid, is a mixture of perchlorate and bisulphate of potassa; and by washing it with cold water, the bisulphate is dissolved, and the perchlorate is left. Perchloric acid may be prepared from this salt by mixing it in a retort with half its weight of sulphuric acid, diluted with one-third of water, and applying heat to the mixture. At the temperature of about 284° F. white vapours rise, which condense as a colourless liquid in the receiver. This is a solution of perchloric acid.

The existence of perchloric acid was first ascertained by Count Stadion, who found it to be a compound of 2 volumes or 1 eq. of chlorine and 7 of oxygen; and this view of its constitution has been confirmed by Gay-Lussac, Serullas, and Mitscherlich. (An. de Ch. et Ph. viii. ix. xlvi. 297, and xlix. 113.) According to Serullas, it is a very stable compound: it may be heated with hydrochloric or sulphuric acid without change, does not set fire to organic substances, and is not decomposed by alcohol. When concentrated it has a density of 1·65, in which state it emits vapour when exposed to the air, absorbs hygrometric moisture powerfully, and boils at 392° F. By admixture with strong sulphuric acid and distilling, Serullas obtained it in the solid form, both massive and in elongated prisms. It hisses when thrown into water, like red-hot iron when quenched.

Of all the salts of perchloric acid, that with potassa is the most insoluble, requiring 65 times its weight of water at 60° for solution. This salt is readily and safely formed by adding chlorate of potassa, well dried and in fine powder, in small portions at a time, to an equal weight of concentrated sulphuric acid, gently warmed in an open vessel. The chlorous acid gas escapes without danger, and the chlorate is entirely converted into perchlorate and bisulphate of potassa, the latter of which, being very soluble, is easily removed by cold water, Serullas finds that chlorate of potassa, when decomposed by a low heat, is converted into chloride of potassium and perchlorate of potassa; but the temperature must be carefully managed, otherwise the perchlorate itself would be resolved into oxygen and chloride of potassium. The perchlorate thus produced is purified by solution in hot water and crystallization. It is distinguished from chlorate of potassa by not acquiring a yellow tint on the addition of hydrochloric acid. The primary form of its crystals, according to Mitscherlich, is a right rhomboidal prism, isomorphous with permanganate of potassa.

The eq. of the acid is 91·42; symb. $Cl + 7O$, $\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{Cl}$, or ClO_7.

According to Millon, the compounds of chlorine and oxygen are seven in number. In addition to the four above described, he admits the existence of the three compounds, ClO_3, which he calls chlorous acid, Cl_3O_{13}, chlorochloric acid, and Cl_3O_{17}, chloroperchloric acid. These compounds have properties very similar to those of hypochloric acid, and resemble each other so much as only to be distinguished by the products of their decomposition.

The following table exhibits Millon's views:—

Hypochlorous Acid	ClO.				
Chlorous Acid	ClO_3.				
Hypochloric Acid	ClO_4	=	Cl_4O_{16}	=	$3ClO_3 + ClO_7$.
Chloric Acid	ClO_5	=	Cl_2O_{10}	=	$ClO_3 + ClO_7$.
Chlorochloric Acid	Cl_3O_{13}	=			$2ClO_3 + ClO_7$.
Chloroperchloric Acid	Cl_3O_{17}	=			$ClO_3 + 2ClO_7$.
Perchloric Acid	ClO_7.				

The acids ClO and ClO_3 yield permanent salts with bases; the acids ClO_4, Cl_3,O_{13}, and Cl_3O_{17}, when acted on by alkalies, yield a mixture of chlorate and chlorite (the acid in the latter being ClO_3), and the proportions are different in each case.

It will be observed that Millon admits only three distinct and independent acids, namely ClO, ClO_3, and ClO_7, and he considers all the rest as made up of the two latter in varying proportions. This explains the products of their action on alkalies, and, in the case of chloric acid, enables us to see how its salts when heated are resolved into perchlorates and chlorides. On this view, chlorate of potash is $KO,ClO_7 + KO,ClO_3 = 2(KO,ClO_5)$; and when heated, it is the latter salt, KO,ClO_3 which gives off oxygen, while KCl, chloride of potassium, is left with the unchanged perchlorate, KO,ClO_7.

But it is difficult to believe that chlorate of potash is such a double salt; it is more probable that is truly a compound of the acid ClO_5, but that under the influence of heat, 2 eq. undergo the above change. Millon's view, however, applies well to the other acids, ClO_4, Cl_3O_{13}, and Cl_3O_{17}, which all possess bleaching and explosive properties, and consequently have probably an analogous constitution. The paper of Millon will be found in the Annales de Chimie et de Physique for 1843.

Quadrochloride of Nitrogen.—Hist. and Prep.—This compound was discovered by Dulong in 1811. Its elements have a feeble mutual affinity, and do not unite when presented to each other in their gaseous form. The condition which leads to their union is the decomposition of ammonia by chlorine, during which hydrochloric acid is generated by chlorine combining with the hydrogen of ammonia; while the nitrogen of that alkali, in its nascent state, enters into combination with another portion of chlorine. A convenient mode of preparing the quadrochloride of nitrogen is the following :—An ounce of hydrochlorate of ammonia is dissolved in 12 or 16 ounces of hot water; and when the solution has cooled to the temperature of 90°, a glass bottle with a wide mouth, full of chlorine, is inverted in it. The solution gradually absorbs the chlorine, and acquires a yellow colour ; and in about 20 minutes globules of a yellow fluid are seen floating like oil upon its surface, which, after acquiring the size of a small pea, sink to the bottom of the liquid. The drops of the chloride, as they descend, should be collected in a small saucer of lead, placed for that purpose under the mouth of the bottle. It is also readily obtained by suspending a fragment of sal-ammoniac in a solution of hypochlorous acid.

Prop.—It is one of the most explosive compounds yet known, having been the cause of serious accidents both to its discoverer and to Davy. (Phil. Trans., 1813; An. de Ch. lxxxvi.) Its specific gravity is 1·653. It does not congeal in the intense cold produced by a mixture of snow and salt. It may be distilled at 160° ; but at a temperature between 200° and 212° it explodes. It appears from the investigation of Messrs. Porrett, Wilson, and Kirk, that its mere contact with some substances of a combustible nature causes detonation even at common temperatures. This result ensues particularly with oils, both volatile and fixed. I have never known olive oil fail in producing the effect. The products of the explosion are chlorine and nitrogen. (Nicholson's Journal, xxxiv.)

Sir H. Davy analyzed chloride of nitrogen by means of mercury, which unites with chlorine, and liberates the nitrogen. He inferred from his analysis that its elements are united in the proportion of four measures of chlorine to one of nitrogen ; and it hence follows, that, by weight, it consists of 4 eq. of chlorine and 1 eq. of nitrogen.

Perchloride of Carbon.—Hist. and Prep.—The discovery of this compound is due to Mr. Faraday. When olefiant gas (a compound of carbon and hydrogen) is mixed with chlorine, combination takes place between them, and an oil-like liquid is generated, which consists of chlorine, carbon, and hydrogen. On exposing this liquid in a vessel full of chlorine gas to the direct solar rays, the chlorine acts upon and decomposes the liquid, hydrochloric acid is set free, and the carbon, at the moment of separation, unites with the chlorine. (Phil. Trans., 1821.)

Prop.—Perchloride of carbon is solid at common temperatures, has an aromatic odour approaching to that of camphor, is a non-conductor of electricity, and refracts light very powerfully. Its sp. gr. is exactly double that of water. It fuses at 320°, and after fusion it is colourless and very transparent. It boils at 360°, and may be distilled without change, assuming a crystalline arrangement as it condenses. It is sparingly soluble in water, but dissolves in alcohol and ether, especially by the aid of heat. It is soluble also in fixed and volatile oils.

It burns with a red light when held in the flame of a spirit-lamp, giving out acid vapours and smoke ; but the combustion ceases as soon as it is withdrawn from the flame. It burns vividly in oxygen gas. Alkalies do not act upon it ; nor is it changed by the stronger acids, such as the hydrochloric, nitric, or sulphuric acids, even with the aid of heat. When its vapour, mixed with hydrogen, is transmitted through a red-hot tube, charcoal is separated, and hydrochloric acid gas evolved. On passing its vapour over the peroxides of metals, such as that of mercury and copper, heated to redness, a chloride of the metal and carbonic acid are generated. Protoxides, under the same treatment, yield carbonic oxide gas and metallic chlorides. Most of the metals decompose it also at the temperature of ignition, uniting with its chlorine, and causing deposition of charcoal.

The composition of the perchloride of carbon was inferred by Faraday from the proportions of chlorine and olefiant gas employed in its production, and from the quantity of chloride of copper and carbonic acid generated when its vapour was transmitted over oxide of copper at a red heat.

Its eq. is 118·50 ; symb. $2C + 3Cl$, or C_2Cl_3.

Protochloride of Carbon.—When the vapour of the perchloride is passed through a red-hot glass or porcelain tube, filled with fragments of rock crystal, to increase the quantity of heated surface, partial decomposition occurs, chlorine gas escapes, and a vapour which, analyzed by Faraday by means of oxide of copper, proved to be protochloride of carbon. At common temperatures it is a limpid colourless liquid, which has a density of 1·5526, does not congeal at 0° F., and at 160° or 170° is converted into vapour. It may be distilled repeatedly without change; but when exposed to a red heat, some of it is resolved into its elements. In its chemical relations it is very analogous to perchloride of carbon.

Its eq. is 41·54 ; symb. $C + Cl$, or $C\,Cl$.

Dichloride of Carbon.—The first sample of this substance yet obtained was brought from Sweden by M. Julin, and is said to have been formed during the distillation of nitric acid from crude nitre and sulphate of iron. It occurs in small, soft, adhesive fibres, of a white colour, which have a peculiar odour, somewhat resembling spermaceti. It fuses on the application of heat, and boils at a temperature between 350° and 450° F. At 250° it sublimes slowly, and condenses again in the form of long needles. It is insoluble in water, acids, and alkalies, but is dissolved by hot oil of turpentine or by alcohol, and forms acicular crystals as the solution cools. It burns with a red flame, emitting much smoke and fumes of hydrochloric acid gas. It has since been obtained among the products of the action of chlorine, aided by light, on some organic compounds.

The nature of this substance is shewn by the following circumstances:—When its vapour is exposed to a red heat, evolution of chlorine gas ensues, and charcoal is deposited. A similar deposition of charcoal is produced by heating it with phosphorus, iron, or tin; and a chloride is formed at the same time. Potassium burns vividly in its vapour with formation of chloride of potassium and separation of charcoal. On detonating a mixture of its vapour with oxygen gas over mercury, a chloride of that metal and carbonic acid are generated. By these means Phillips and Faraday ascertained its composition. (An. of Phil. xviii. 150.) Its eq. is 47·66; symb. $2C + Cl$, or C_2Cl.

Dichloride of Sulphur.—This compound was discovered in the year 1804 by Thomson,* and was afterwards examined by Berthollet.† It is most conveniently prepared by passing a current of chlorine gas over flowers of sulphur gently heated, until nearly all the sulphur disappears. Direct combination ensues, and the product, distilled off from uncombined sulphur, is obtained under the form of a liquid which appears red by reflected, and yellowish-green by transmitted light. Its density is 1·687. It is volatile below 200°, boils at 280°, yielding vapour which has a density of 4·70, and condenses again without change in cooling. When exposed to the air it emits acrid fumes, which irritate the eyes powerfully, and have an odour somewhat resembling sea-weed, but much stronger. Dry litmus paper is not reddened by it, nor does it unite with alkalies. It acts with energy on water: mutual decomposition ensues, with formation of hydrochloric and hyposulphurous acids, and deposite of sulphur, by which the water is rendered cloudy. From a recent analysis by Rose, it consists of 35·42 parts or 1 eq. of chlorine and 32·2 parts or 2 eq. of sulphur. (Pog. An. xxi. 431.)

Its eq. is 67·62; symb. $2S + Cl$, or S_2Cl.

Rose maintains that the preceding is the only chloride of sulphur, arguing that the chloride analyzed by Davy was merely dichloride of sulphur holding chlorine in solution. Dumas, on the other hand, contends, that when sulphur is acted on by excess of chlorine, a chloride of sulphur is really obtained, which is apt to retain traces of the dichloride, and can only be purified by repeated distillation at about 140° F. This chloride is a liquid of a deep reddish-brown tint, and has a density of 1·62. It boils at 147°, and the density of its vapour is between 3·67 and 3·70. By decomposition in water it should yield hydrochloric and hyposulphurous acids. Its composition is SCl; eq. 51·52. (An. de Ch. et Ph. xlix. 205.)

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* Nicholson's Journal, vol. vi.

† Mémoires d'Arcueil.

Perchloride of Phosphorus.—There are two definite compounds of chlorine and phosphorus, the nature of which was first satisfactorily explained by Davy. (Elements, p. 290.) When phosphorus is introduced into a jar of dry chlorine, it inflames, and on the inside of the vessel a white matter collects, which is *perchloride of phosphorus.* It is very volatile, a temperature much below 212° being sufficient to convert it into vapour. Under pressure it may be fused, and it yields transparent prismatic crystals in cooling.

Water and perchloride of phosphorus mutually decompose each other; and the sole products are hydrochloric and phosphoric acids. Now, in order that these products should be formed, consistently with the constitution of phosphoric acid, as stated at page 257, the perchloride must consist of 31·4 parts or 2 eq. of phosphorus, and 177·1 parts or 5 eq. of chlorine. One eq. of the chloride and 5 eq. of water will then mutually decompose each other without any element being in excess, and yield 1 eq. of phosphoric, and 5 eq. of hydrochloric acid. This proportion is not far from the truth; for, according to Davy, one grain of phosphorus is united in the perchloride with six of chlorine.

Its eq. is 206·4; symb. $2P + 5Cl$, or P_2Cl_5.

Sesquichloride of Phosphorus may be made either by heating the perchloride with phosphorus, or by passing the vapour of phosphorus over corrosive sublimate contained in a glass tube. It is a clear liquid, like water, of sp. gr. 1·45; emits acid fumes when exposed to the air, owing to the decomposition of watery vapour; but when pure it does not redden dry litmus paper. On mixing it with water mutual decomposition ensues, heat is evolved, and a solution of hydrochloric and phosphorous acids is obtained. It hence appears to consist of 31·4 parts or 2 eq. of phosphorus, and 106·26 parts or 3 eq. of chlorine. Its eq. is 137·66; symb. $2P + 3Cl$, or P_2Cl_3.

When hydrosulphuric acid gas is transmitted through a vessel containing perchloride of phosphorus, hydrochloric acid is disengaged, and a liquid produced, which, according to Serullas, is a compound of three equivalents of chlorine, one of phosphorus, and one of sulphur. (An. de Ch. et Ph. xlii. 25.)

Chlorocarbonic Acid Gas.—Hist. and Prep.—This compound was discovered in 1812 by John Davy, who described it in the Philosophical Transactions for that year, under the name of *phosgene gas.* (From *φως light*, and *γενναειν to produce.*) It is made by exposing a mixture of equal measures of dry chlorine and carbonic oxide gases to sunshine, when rapid but silent combination ensues, and they contract to one-half their volume. Diffused daylight also effects their union slowly; but they do not combine at all when the mixture is wholly excluded from light.

Prop.—It is colourless gas, has a strong odour, and reddens dry litmus paper. It combines with four times its volume of ammoniacal gas, forming a white solid salt; so that it possesses the characteristic property of acids. It is decomposed by contact with water. One equivalent of each compound undergoes decomposition; and, as the hydrogen of the water unites with chlorine, and its oxygen with carbonic oxide, the products are carbonic and hydrochloric acids. When tin is heated in this gas, chloride of tin is generated, and carbonic oxide gas set free, which occupies exactly the same space as the chlorocarbonic acid which was employed. A similar change occurs when it is heated in contact with antimony, zinc, or arsenic.

As chlorocarbonic acid gas contains its own volume of each of its constituents, it follows that 100 cubic inches of that gas at the standard temperature and pressure must weigh 106·806 grains; namely, 76·599 of chlorine added to 30·207 of carbonic oxide. Its sp. gr. is therefore 3·4427, and it consists of 35·42 or 1 eq. of chlorine, and 14·15 parts or 1 eq. of carbonic oxide.

Its eq. is 49·54; symb. $C + O + Cl$, or $COCl$.

Terchloride of Boron.—Davy noticed that recently prepared boron takes fire spontaneously in an atmosphere of chlorine, and emits a vivid light; but he did not examine the product. Berzelius remarked, that if the boron has been previously heated, whereby it is rendered more compact, the combustion does not take place till heat is applied. This observation led him to expose boron, thus rendered dense, in a glass tube to a current of dry chlorine; and to heat it gently as soon as the atmospheric air was completely expelled, in order to commence the combustion. The resulting compound proved to be a colourless gas; and on collecting it over mercury, which absorbed free chlorine, he procured the chloride of boron in a state of purity. This gas is rapidly absorbed by water; but double decomposition takes place at the same instant, giving rise to hydrochloric and boracic acids as the sole products: from this fact is inferred the composition of the chloride; for 1 eq. of terchloride of boron or $B + 3Cl$, and 3 eq. of water or $3(H + O)$, correspond to 1 eq. of boracic acid or $B + 3O$, and 3 eq. of hydrochloric acid or $3(H + Cl)$. The watery vapour of the atmosphere occasions a similar change; so that when the gas is mixed with air containing hygrometric moisture, a dense white cloud is produced.

The sp. gr. of the gas, according to Dumas, is 3·942. It is soluble in alcohol, and communicates to it an ethereal odour, apparently by the action of hydrochloric acid. It unites with ammoniacal gas, forming a fluid volatile substance, the nature of which is unknown. (Annals of Phil. xxvi. 129.)

Dumas finds that chloride of boron may be generated by the action of dry chlorine on a mixture of charcoal and boracic acid, heated to redness in a porcelain tube. Although neither charcoal nor chlorine can, when acting alone, decompose boracic acid, they do so readily by their united effort. According to Dumas, two volumes of chloride of boron, and three of carbonic oxide gas are formed. From these data chloride of boron may be considered as composed of 3 eq. vol. of chlorine and 1 eq. vol. of boron condensed into two volumes. Its sp. gr. is 4·079. (Dumas.)

Despretz also appears to have invented a similar process. (Philos. Magazine and Annals, i. 469.)

Its eq. is 117·16; eq. vol. $= 200$; symb. $B + 3Cl$, or BCl_3.

Terchloride of Silicon.—When silicon is heated in a current of chlorine gas, it takes fire, and is rapidly volatilized. The product of the combustion condenses into a liquid, which appears to be naturally colourless, but to which an excess of chlorine communicates a yellow tint. This fluid is very limpid and volatile, and evaporates almost instantaneously in open vessels in the form of a white vapour. It boils at 124°, and bears a cold of zero without becoming solid. It has a suffocating odour not unlike that of cyanogen, and when put into water is converted into hydrochloric and silicic acids, the latter being easily obtained in a gelatinous form. (Berzelius.)

It may also be prepared by the method proposed by Oersted, which has been so successfully applied in the formation of other chlorides. It consists in mixing about equal parts of hydrated silicic acid and starch into a paste with oil, heating the mass in a covered crucible so as to char the starch, introducing the mixture in fragments into a porcelain tube, and then transmitting through it a current of dry chlorine gas while the tube is kept at a red heat. The chlorine unites with silicium, while the charcoal and oxygen combine. The volatile chloride is then agitated with mercury to separate the free chlorine, and purified by distillation.

Its eq. is 128·76; symb. $Si + 3Cl$, or $SiCl_3$.

Chloro-nitrous Gas.—When fused chloride of sodium, potassium, or calcium, in powder, is treated with as much strong nitric acid as is sufficient to wet it, mutual decomposition ensues, and a new gas composed of chlorine and binoxide of nitrogen is generated. Its discoverer, Mr. E. Davy, describes it as a gas of a pale reddish yellow colour, of an odour similar to that of chlorine, though less pungent, and possessed of bleaching properties. It fumes on exposure to the air, and is freely absorbed by water. It is decomposed by sulphur, phosphorus, mercury, and most metals, and by substances in general which have an affinity for chlorine. It consists, according to Davy, of equal volumes of chlorine and binoxide of nitrogen, united without any condensation.

In the mutual decomposition of chloride of sodium and nitric acid, the products appear to be chloro-nitrous and chlorine gases, and nitrate of soda. Their formation must obviously depend on sodium being oxidized at the expense of nitric acid, while part of the chlorine unites, at the moment of separation from the sodium, with binoxide of nitrogen. (Phil. Mag. ix. 355.) Theoretically, it should be mixed with twice its volume of chlorine, the presence of which must materially obscure the properties of the new gas.

ON THE NATURE OF CHLORINE.

The change of opinion which has gradually taken place among chemists concerning the nature of chlorine, is a remarkable fact in the history of the science. The hypothesis of Berthollet, unfounded as it is, prevailed at one time universally. It explained phenomena so satisfactorily, and in a manner so consistent with the received chemical doctrine, that for some years no one thought of calling its correctness into question. A singular reverse, however, has taken place; and this hypothesis, though it has not hitherto been rigidly demonstrated to be erroneous, has within a short period been generally abandoned, even by persons who, from having adopted it in early life, were prejudiced in its favour. The reason of this will readily appear on comparing it with the opposite theory, and examining the evidence in favour of each.

Chlorine, according to the new theory, is maintained to be a simple body, because, like oxygen, hydrogen, and other analogous substances, it cannot be resolved into more simple parts. It does not indeed follow that a body is simple because it has not hitherto been decomposed; but as chemists have no other mode of estimating the elementary nature of bodies, they must necessarily adopt this one, or have none at all. Hydrochloric acid, by the same rule, is considered to be a compound of chlorine and hydrogen. For when exposed to the agency of galvanism, it is resolved into these substances; and by mixing the two gases in due proportion, and passing an electric spark through the mixture, hydrochloric acid gas is the product. Chemists have no other kind of proof of the composition of water, of potassa, or of any other compound.

Very different is the evidence in support of the theory of Berthollet. According to that view, hydrochloric acid gas is composed of *absolute muriatic acid* and water or its elements; chlorine consists of *absolute muriatic acid* and oxygen; and *absolute muriatic acid* is a compound of a certain unknown base and oxygen gas. Now all these propositions are gratuitous. For, in the first place, hydrochloric acid gas has not been proved to contain water. Secondly, the assertion that chlorine contains oxygen is opposed to direct experiment, the most powerful deoxidizing agents having been unable to elicit from that gas a particle of oxygen. Thirdly, the existence of such a substance as *absolute muriatic acid* is wholly without proof, and therefore its supposed base is also imaginary.

But this is not the only weak point of the doctrine. Since chlorine is admitted by this theory to contain oxygen, it was necessary to explain how it happens that no oxygen can be separated from it. For instance, on exposing chlorine to a powerful galvanic battery, oxygen gas does not appear at the positive pole, as occurs when other oxidized bodies are subjected to its action; nor is carbonic acid or carbonic oxide evolved, when chlorine is conducted over ignited charcoal. To account for the oxygen not appearing under these circumstances, it was assumed that *absolute muriatic acid* is unable to exist in an uncombined state, and therefore cannot be separated from one substance except by uniting with another. This supposition was thought to be supported by the analogy of certain compounds, such as nitric and oxalic acids, which appear to be incapable of existing except when combined with water or some other substance. The analogy, however, is incomplete; for the decomposition of such compounds, when an attempt is made to procure them in an insulated state, is manifestly owing to the tendency of their elements to enter into new combinations.

Admitting the various assumptions which have been stated, most of the phenomena receive as consistent an explanation by the old as by the new theory. Thus, when hydrochloric acid gas is resolved by galvanism into chlorine and hydrogen, it may be supposed that *absolute muriatic acid* attaches itself to the oxygen of the water, and forms chlorine; while the hydrogen of the water goes to the opposite pole of the battery. When chlorine and hydrogen enter into combination, the oxygen of the former may be said to unite with the latter; and that hydrochloric acid gas is generated by the water so formed combining with the *absolute muriatic acid* of the chlorine. The evolution of chlorine, which ensues on mixing hydrochloric acid and peroxide of manganese, is explained on the supposition that *absolute muriatic acid* unites directly with the oxygen of the black oxide of manganese.

It will not be difficult, after these observations, to account for the preference shewn to the new theory. In an exact science, such as chemistry, every step of which is required to be matter of demonstration, there is no room to hesitate between two modes of reasoning, one of which is hypothetical, and the other founded on experiment. Nor is there, in the present instance, temptation to deviate from the strict logic of the science; for there is not a single phenomenon which may not be fully explained on the new theory, in a manner quite consistent with the laws of chemical action in general.

It was supposed, indeed, at one time, that the sudden decomposition of water, occasioned by the action of that liquid on the compounds of chlorine with some simple substances, constitutes a real objection to the doctrine; but it will afterwards appear, that the acquisition of new facts has deprived this argument of all its force. While nothing therefore can be gained, much may be lost by adopting the doctrine of Berthollet. If chlorine is regarded as a compound body, the same opinion, though in direct opposition to the result of observation, ought to be extended to iodine and bromine; and as other analogous substances may hereafter be discovered, in regard to which a similar hypothesis will apply, it is obvious that this view, if proper in one case, may legitimately be extended to others. One encroachment on the method of strict induction would consequently open the way to another, and thus the genius of the science would eventually be destroyed.

An able attempt was made some years ago by the late Dr. Murray, to demonstrate the presence of water or its elements as a constituent part of hydrochloric acid gas, and thus to establish the old theory to the subversion of the new. The arguments which he used, though plausible and ingenious, were successfully combated by Sir H. and Dr. Davy. The only experiment which strictly bears upon the question —that, namely, where hydrochloric acid and ammoniacal gases were mixed together—goes far to demonstrate the absence of combined water in hydrochloric acid gas, and therefore to establish the views of Davy.*

SECTION XIII.

IODINE.

Hist.—Iodine was discovered in the year 1812 by M. Courtois, a manufacturer of saltpetre at Paris. In preparing carbonate of soda from the ashes of sea-weeds, he observed that the residual liquor corroded metallic vessels powerfully; and on investigating the cause of the corrosion, he noticed that sulphuric acid threw down a dark-coloured matter, which was converted by the application of heat into a beautiful violet vapour. Struck with its appearance, he gave some of the substance to M. Clément, who recognized it as a new body, and in 1813 described some of its leading properties in the Royal Institute of France. Its real nature was soon after determined by Gay-Lussac and Davy, each of whom proved that it is a simple non-metallic substance, exceedingly analogous to chlorine.*

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* In Nicholson's Journal, vols. xxxi., xxxii., and xxxiv. Edinburgh Philos. Trans., vol. viii., and Philos. Trans. for 1818.

Iodine is frequently met with in nature in combination with potassium or sodium. Under this form it occurs in many salt and other mineral springs, both in England and on the Continent. It has been detected in the water of the Mediterranean, in the oyster and some other marine molluscous animals, in sponges, and in most kinds of sea-weed. In some of these productions, such as the *Fucus serratus* and *Fucus digitatus*, it exists ready formed, and according to Fyfe (Edin. Philos. Journal, i. 254) may be separated by the action of water; but in others it can be detected only after incineration. Marine animals and plants doubtless derive from the sea the iodine which they contain. Vauquelin found it also in the mineral kingdom, in combination with silver. (An. de Ch. et Ph. xxix.)

Prep.—The iodine of commerce is procured from the impure carbonate of soda, called kelp, which is prepared in large quantity on the northern shores of Scotland, by incinerating sea-weeds. The kelp is employed by soap-makers for the preparation of carbonate of soda; and the dark residual liquor remaining after that salt has crystallized, contains a considerable quantity of iodine, combined with sodium or potassium. By adding a sufficient quantity of sulphuric acid, hydriodic acid is first generated, and then decomposed. The iodine sublimes when the solution is boiled, and may be collected in cool glass receivers. A more convenient process is to employ a moderate excess of sulphuric acid, and then add to the mixture some peroxide of manganese, which acts on hydriodic in the same way as on hydrochloric acid. (Phil. Mag., Dr. Ure.) Another method, proposed by Soubeiran, is by adding to the ley from kelp a solution made with the sulphates of protoxides of copper and iron in the ratio of one of the former to $2\frac{1}{4}$ of the latter, as long as a precipitate appears. The diniodide of copper is thus thrown down; and it may be decomposed either by peroxide of manganese alone, or by manganese and sulphuric acid. By means of the former, the iodine passes over quite dry; but a strong heat is requisite.

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* The original papers on this subject are in the Annales de Chimie, vols. lxxxviii., xc., and xci.; and in the Philos. Trans. for 1814 and 1815.

Prop.—Iodine, at common temperatures, is a soft friable opaque solid of a bluish-black colour, and metallic lustre. It occurs usually in crystalline scales, having the appearance of micaceous iron ore; but it sometimes crystallizes in large rhomboidal plates, the primitive form of which is a rhombic octohedron. The crystals are best prepared by exposing to the air a solution of iodine in hydriodic acid. Its sp. gr., according to Gay-Lussac, is 4·948; but Thomson found it only 3·0844. At 225° it is fused, and enters into ebullition at 347°; but when moisture is present, it is sublimed rapidly even below the degree of boiling water, and suffers a gradual dissipation at low temperatures. Its vapour is of an exceedingly rich violet colour, a character to which it owes the name of *Iodine.* (From 'Ιώδης, violet-coloured.) This vapour is remarkably dense, its sp. gr. by calculation being 8·7011, or 8·716, as directly observed by Dumas. Hence 100 cubic inches, at the standard temperature and pressure, must weigh 269·84 grains.

It is a non-conductor of electricity, and, like oxygen and chlorine, is a —electric. It has a very acrid taste, and its odour is almost exactly similar to that of chlorine, when much diluted with air. It acts energetically on the animal system as an irritant poison, but is employed medicinally in very small doses with advantage.

It is very sparingly soluble in water, requiring about 7000 times its weight of that liquid for solution. It communicates, however, even in this minute quantity, a brown tint to the menstruum. Alcohol and ether dissolve it freely, and the solution has a deep reddish-brown colour.

Iodine possesses an extensive range of affinity. It destroys vegetable colours, though in a much less degree than chlorine. It manifests little disposition to combine with metallic oxides; but it has a strong attraction for the pure metals, and for most of the simple non-metallic substances, producing compounds which are termed *Iodides* or *Iodurets.* It is not inflammable; but under favourable circumstances may, like chlorine, be made to unite with oxygen. A solution of the pure alkalies acts upon it and gives rise to decomposition of water; whether an hypo-iodite and iodide are first produced, as in the case of chlorine, has not yet been determined, but on the application of heat an iodate and iodide are formed.

Pure iodine is not influenced chemically by the imponderables. Exposure to the direct solar rays, or to strong shocks of electricity, does not change its nature. It may be passed through red-hot tubes, or over intensely ignited charcoal, without any appearance of decomposition; nor is it affected by the agency of galvanism. Chemists, indeed, are unable to resolve it into more simple parts, and consequently it is regarded as an elementary principle.

The violet hue of the vapour of iodine is for many purposes a sufficiently sure indication of its presence. A far more delicate test, however, was discovered by Colin and Gaultier de Claubry. They found that iodine has the property of uniting with starch, and of forming with it a compound insoluble in cold water, which is recognized with certainty by its deep blue colour. This test, according to Stromeyer, is so delicate, that a liquid containing 1-450,000th of its weight of iodine receives a blue tinge from a solution of starch. Two precautions should be observed to insure success. In the first place, the iodine must be in a free state; for it is the iodine itself only, and not its compounds, which unites with starch. Secondly, the solution should be quite cold at the time of adding the starch; for hot water dissolves the blue compound, and forms a colourless solution.

Berzelius determined the equivalent of iodine by exposing fused iodide of silver to a current of chlorine gas, whereby the iodine was expelled and chloride of silver generated. Through the known composition of chloride of silver he inferred that of the iodide, and thence found the eq. of iodine. It is 126·3; eq. vol. = 100; symb. I.

The composition of the compounds of iodine described in this section is as follows:—

	Iodine.				Equiv.	Formulæ.
Hydriodic Acid .	126·3	1 eq. +	1	1 eq. hydrogen	= 127·3	$H+I$ or HI.
Oxide of Iodine .	Composition unknown.					
Iodous Acid .						
Iodic Acid . .	126·3	1 eq. +	40	5 eq. oxygen	= 166·3	IO_5.
Periodic Acid . .	126·3	1 eq. +	56	7 eq. do.	= 182·3	IO_7.
Protochloride of Iodine	126·3	1 eq. +	35·42	1 eq. chlorine	= 161·72	ICl.
Terchloride do. .	126·3	1 eq. +	106·26	3 eq. do.	= 232·56	ICl_3.
Perchloride do.	Composition doubtful.					
Protiodide of Phos. .	126·3	1 eq. +	15·7	1 eq. phosph.	= 142·0	PI.
Sesquiodide do. .	378·9	3 eq. +	31·4	2 eq. do.	= 410·3	P_2I_3.
Periodide do. .	631·5	5 eq. +	31·4	2 eq. do.	= 662·9	P_2I_5.
Iodide of Sulphur .	Composition unknown.					
Iodide of Carbon .	Composition unknown.					
Periodide of Carbon	Composition unknown.					
Teriodide of Nitrogen .	378·9	3 eq. +	14·15	1 eq. nitrogen	= 393·05	NI_3.

Hydriodic Acid.—Prep.—This compound is formed by the direct union of its elements, when a mixture of hydrogen gas and iodine vapour are transmitted through a porcelain tube at a red heat. A more convenient process, and by which it is obtained in a pure state, is, by the action of water on the periodide of phosphorus. Any convenient quantity of the iodide is put into a small glass retort, together with a little water, and a gentle heat is applied. Mutual decomposition ensues; the oxygen of the water unites with phosphorus, and its hydrogen with iodine, giving rise to the formation of phosphoric and hydriodic acids, the latter of which passes over in the form of a colourless gas. The preparation of the iodide requires care; since phosphorus and iodine act so energetically on each other by mere contact, that the phosphorus is generally inflamed, and a great part of the iodine expelled in the form of vapour. This inconvenience is avoided by putting the phosphorus into a tube sealed at one end, about twelve inches long, displacing the air by a current of dry carbonic acid gas, then gradually adding the iodine, and promoting the action towards the close by a gentle heat. The materials should be well dried with bibulous paper, and the iodide preserved in a well-stopped dry vessel; for even atmospheric humidity gives rise to copious white fumes of hydriodic acid. The proportions usually employed are one part of phosphorus to about twelve of iodine. Another process has been recommended by F. d'Arcet, which consists in evaporating hypophosphorous acid until it begins to yield phosphuretted hydrogen, mixing it with an equal weight of iodine, and applying a gentle heat. Hydriodic acid gas of great purity is then rapidly disengaged; its production depending, as in the former process, on the decomposition of water.

Prop.—Hydriodic acid gas has a very sour taste, reddens vegetable blue colours without destroying them, produces dense white fumes when mixed with atmospheric air, and has an odour similar to that of hydrochloric acid gas. The salts which it forms with alkalies are sometimes called *hydriodates*, but are in reality *iodides* of the metals. Like hydrochloric acid gas, it cannot be collected over water; for that liquid dissolves it in large quantity.

It is decomposed by several substances which have a strong affinity for either of its elements. Thus oxygen gas, when heated with it, unites with its hydrogen, and liberates the iodine. Chlorine effects the decomposition instantly; hydrochloric acid gas is produced, and the iodine appears in the form of vapour. With strong nitrous acid it takes fire, and the vapour of iodine is set free. It is also decomposed by mercury. The decomposition begins as soon as hydriodic acid gas comes in contact with mercury, and proceeds steadily, and even quickly, if the gas is agitated, till nothing but hydrogen remains. Gay-Lussac ascertained by this method that 100 measures of hydriodic acid gas contain precisely half their volume of hydrogen. Assuming it to consist of equal volumes of hydrogen gas and iodine vapour united without any condensation, then, since

	Grains.
50 cubic inches of the Vapour of Iodine weigh . . .	134·9200
50 do. Hydrogen Gas	1·0684
100 cubic inches of Hydriodic Acid Gas should weigh . .	135·9884.

These numbers are obviously in the ratio of 1 to 126·3, the eq. of iodine and hydrogen. On the same principles the density of the gas should be 4·3850, which is probably more correct than 4·443, the number found experimentally by Gay-Lussac. (An. de Ch. xci. 16.) From these coincidences there is no doubt that 100 measures of hydriodic acid gas contain 50 measures of hydrogen gas and 50 of the vapour of iodine.

When the gas is conducted into water till that liquid is fully charged with it, a colourless acid solution is obtained, which emits white fumes on exposure to the air, and has a sp. gr. of 1·7. It may be prepared also by transmitting a current of hydrosulphuric acid gas through water in which iodine in fine powder is suspended; or by adding sulphuric acid in atomic proportion to a solution of iodide of barium. (Glover.) The iodine, from having a greater affinity than sulphur for hydrogen, decomposes the hydrosulphuric acid; and hence sulphur is set free, and hydriodic acid produced. As soon as the iodine has disappeared and become colourless, it is heated for a short time to expel the excess of hydrosulphuric acid, and subsequently filtered to separate free sulphur.

The solution is readily decomposed. On exposure during a few hours to the atmosphere, the oxygen of the air forms water with the hydrogen of the acid, and sets iodine free. The solution is found to have acquired a brown tint, from the presence of uncombined iodine, and a blue colour is occasioned by the addition of starch. Nitric and sulphuric acid likewise decompose it by yielding oxygen, the former being at the same time converted into nitrous, and the latter into sulphurous acid. Chlorine unites directly with the hydrogen of the hydriodic acid, and hydrochloric acid is formed. The separation of iodine in all these cases may be proved in the way just mentioned. These circumstances afford a sure test of the presence of hydriodic acid, whether free or in combination with alkalies. All that is necessary is to mix a cold solution of starch with the liquid, previously concentrated by evaporation, if necessary, and then add a few drops of strong sulphuric acid. A blue colour will make its appearance if hydriodic acid is present.

Its eq. is 127·3; eq. vol. $= 200$; symb. $H + I$, or HI.

Oxide of Iodine and Iodous Acid.—On mixing the vapour of iodine and oxygen gas considerably heated, the violet tint of the former disappears, and a yellow matter, of the consistence of solid oil, is generated, which Sementini regards as oxide of iodine; and, if the supply of oxygen be kept up after its formation, it is converted into a yellow liquid, which he supposes to be iodous acid. From the mode in which the process is described, there can scarcely be a doubt that some compound of iodine and oxygen is thus formed; but its composition and properties have not been satisfactorily made out. (Quarterly Journ. of Science, N. S., i. 478.) On dissolving iodine in a rather dilute solution of soda, until the solution begin to acquire a red tint, permanent crystals are obtained by spontaneous evaporation, in six-sided prisms, which dissolve in cold water without change; but, by the action of water moderately heated, or by alcohol, are converted into iodate of soda and iodide of sodium. On the addition of an acid, iodine and iodic acid were set at liberty. From these facts Mitscherlich infers the crystals to be iodite of soda. (An. de Ch. et Ph. xxx. 84.) They are more probably the hypo-iodite.

Iodic Acid.—Hist. and Prep.—This acid was discovered at about the same time by Gay-Lussac and Davy; but the latter first succeeded in obtaining it in a state of perfect purity. When iodine is brought into contact with the euchlorine of Davy, immediate action ensues; the chlorine unites with one portion of iodine, and the oxygen with another, forming two compounds, a volatile orange-coloured matter, chloride of iodine, and a white solid substance, which is *iodic acid.* On applying heat, the former passes off in vapour, and the latter remains. (Phil. Trans. for 1815.) Serullas has obtained it, in the form of hexagonal laminæ, by evaporating in a warm place its solution either in water or in sulphuric or nitric acids. The method which he found most convenient is by forming a solution of iodate of soda in a considerable excess of sulphuric acid, keeping it at a boiling temperature for twelve or fifteen minutes, and then setting it aside to crystallize. (Ann. de Ch. et Ph. xliii. 216.) Iodic acid may also be formed by dissolving perchloride of iodine in water, and gradually adding a large quantity of strong sulphuric acid, a rise of temperature being at the same time prevented by the application of cold. Iodic acid will then be precipitated. The action of strong alcohol on moist perchloride produces the same result: water and the perchloride decomposed, and hydrochloric and iodic acids formed. The latter is left undissolved by the alcohol. Another process, suggested by Mr. Connell of Edinburgh, is by boiling iodine in nitric acid. For this purpose a pure acid, of density 1·5, should be introduced, with about a fifth of its weight of iodine, into a tube sealed at one end, about an inch wide and 15 inches long, and these materials be kept at a boiling temperature for at least twelve hours. As the iodine rises and condenses on the sides of the tube, it should be restored to the liquid, either by agitation or by help of a glass rod. As soon as the iodine disappears, the nitric acid is dissipated by cautious evaporation. It is also obtained, as remarked by Balard, by the oxidizing effect of hypochlorous acid on iodine: the latter unites with the oxygen of the acid, and the chlorine escapes in the gaseous state.

Prop.—This compound, which was termed *oxiodine* by Davy, is *anhydrous iodic acid.* It is a white semitransparent solid, which has a strong astringent sour taste, but no odour. Its sp. gr. is considerable, as it sinks rapidly in sulphuric acid. When heated to the temperature of about 500° F. it is fused, and at the same time resolved into oxygen and iodine. In a dry air it is unchanged; but in a moist atmosphere it absorbs humidity, forming the hydrated acid, and eventually deliquesces. In water it is very soluble, and the solution has a distinct acid reaction: the bleaching power ascribed to it by Davy is said by Hiley not to be a property of pure iodic acid. (Lancet for July, 1833.) On evaporating the solution, a thick mass of the consistence of paste is left, which is hydrous iodic acid; and which, by the cautious application of heat, may be rendered anhydrous. It acts powerfully on inflammable substances. With charcoal, sulphur, sugar, and similar combustibles, it forms mixtures which detonate when heated. It enters into combination with metallic oxides, and the resulting salts are called *iodates.* These compounds, like the chlorates, yield pure oxygen by heat, and deflagrate when thrown on burning charcoal.

Iodic acid forms with the pure alkalies salts which are soluble in water; but with lime, baryta, strontia, and the oxides of lead and silver, it yields compounds of very sparing solubility. It is readily detected by the facility with which it is deoxidized, an effect readily produced by the sulphurous, phosphorous, hydriodic, and hydrosulphuric acids. Iodine in each case is set at liberty, and may be detected as usual by starch. Hydrochloric and iodic acids decompose each other, water and chloride of iodine being generated.

Davy ascertained the composition of iodic acid by determining the quantity of oxygen which the acid loses when decomposed by heat; Gay-Lussac arrived at the same result by heating iodate of potassa, when pure oxygen was given off and iodide of potassium remained. Its eq. is 166·3; symb. $I + 5O$, $\overset{\cdot\cdot\cdot\cdot\cdot}{I}$, or IO_5.

Periodic Acid.—Hist. and Prep.—This compound was discovered by Ammermüller and Magnus. (Pogg. Annalen, xxviii. 514.) When pure soda is mixed with a solution of iodate of soda, and chlorine gas is transmitted into it to saturation, a sparingly soluble white pulverulent salt is generated, which subsides after heating, and, if necessary, concentrating the solution. This salt is a periodate of soda, the production of which appears to depend on the formation of chloride of sodium, and the union of the oxygen of the soda with the iodine of the iodic acid. For each equivalent of periodic acid, 2 eqs. of chloride of sodium should be generated; since the materials IO_5, 2NaO, 2Cl, just suffice for yielding IO_7 and 2NaCl. On dissolving the periodate of soda in dilute nitric acid, and adding nitrate of oxide of silver, the periodate of this oxide of a greenish-yellow colour subsides, which should be washed with water acidulated with nitric acid. This yellow salt is soluble in hot dilute nitric acid, and separates again on cooling in small shining straw-yellow crystals, which by digestion with warm water acquire, without dissolving, a reddish-brown almost black colour. If the nitric acid solution of the yellow salt is so far concentrated by evaporation that it crystallizes while still warm, orange-coloured crystals subside. These three salts are readily analyzed by exposure to a red heat in a glass tube, when iodine and metallic silver, united, remain in the tube, and oxygen gas along with water, when water is present, is expelled. Their composition is as follows:—

	Oxide of Silver.		Periodic Acid.		Water.		Formulæ.
Yellow Salt .	232	2 eq.	182·3	1 eq.	27	3 eq.	IO_7,2AgO,3aq.
Red Salt .	232	2 eq.	182·3	1 eq.	18	2 eq.	IO_7,2AgO,2aq.
Orange Salt .	116	1 eq.	182·3	1 eq.	0		IO_7,AgO.

The two former are therefore hydrated subperiodates of oxide of silver, and the latter a neutral anhydrous periodate. This neutral salt has the peculiarity, that by pure cold water it is converted into the yellow sub-salt, while the water takes up exactly half of its acid without a trace of silver. By this means a pure solution of periodic acid may be obtained.

Prop.—Periodic acid is analogous in composition to perchloric acid, and has decided acid properties. Its solution may be boiled without decomposition, and on evaporation the acid yields crystals, which do not change by exposure to the air. By hydrochloric acid it is reduced to iodic acid with disengagement of chlorine, and the same change will of course be produced by substances which decompose iodic acid. When the heat is increased beyond 212°, (the precise point is not stated,) periodic acid loses oxygen, and iodic acid remains. Thus is periodic more easy of decomposition than iodic acid. Its eq. is 182·3; symb. $I + 7O$, $\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{I}$, or IO_7.

Millon has investigated the subject of the compounds of iodine with oxygen, and is of opinion that the following stages of oxidation exist, although they have not all been obtained in the separate state:—

Iodous Acid . .	$I_2O_6 = 2IO_3$.
Iodic Acid . .	$IO_5 = I_2O_{10} = IO_7 + IO_3$.
Periodic Acid . .	IO_7.
Hypoiodic Acid .	$IO_4 = I_4O_{16} = IO_7 + 3IO_3$.
Subhypoiodic Acid .	$I_5O_{19} = IO_7 + 4IO_3$.

Chlorides of Iodine.—Chlorine is absorbed at common temperatures by dry iodine with evolution of heat, and a solid compound of iodine and chlorine results, which was discovered both by Davy and Gay-Lussac. The colour of the product is orange-yellow when the iodine is fully saturated with chlorine, but is of a reddish-orange if iodine is in excess. It is converted by heat into an orange-coloured liquid, which yields a vapour of the same tint on increase of temperature. It deliquesces in the open air, and dissolves freely in water. Its solution is colourless, very sour to the taste, and reddens vegetable blue colours, but afterwards destroys them. From its acid properties Davy gave it the name of *chloriodic acid.* Gay-Lussac, on the contrary, calls it *chloride of iodine,* conceiving that the acidity of its solution arises from the presence of hydrochloric and iodic acids, which he supposes to be generated by decomposition of water. From the observations of Serullas and Dumas it appears that there exist two compounds of chlorine and iodine, by the different action of which on water the discordant opinions of Davy and Gay-Lussac may be explained.

This subject has lately been examined by Soubeiran. He has distinguished a compound of 3 eq. of chlorine and 1 eq. of iodine, but doubts the existence of the perchloride of iodine of Davy and Gay-Lussac. (Journal de Pharmacie, Feb., 1837.) This compound and a protochloride appear, however, to have been previously described by Kane. (Phil. Mag. x. 430.) The protochloride was obtained by passing a current of chlorine gas into water, in which iodine was diffused. A deep reddish-yellow solution is formed, which gives off fumes irritating to the eyes and nose, has a peculiar smell of both its constituents, and first reddens and then bleaches litmus paper. The terchloride was obtained by repeatedly distilling the protochloride: it may also be procured by adding to the protochloride a strong solution of corrosive sublimate, which throws down iodine. The perchloride is supposed to contain 5 eq. of chlorine and 1 eq. of iodine, from giving rise, when decomposed by water, to hydrochloric and iodic acids.

Teriodide of Nitrogen.—From the weak affinity that exists between iodine and nitrogen, these substances cannot be made to unite directly. But when iodine is put into a solution of ammonia, the alkali is decomposed; its elements unite with different portions of iodine, and thus cause the formation of hydriodic acid and iodide of nitrogen. The latter subsides in the form of a dark powder, which is characterized, like quadrochloride of nitrogen, by its explosive property. It detonates violently as soon as it is dried; and slight pressure, while moist, produces a similar effect. Heat and light are emitted during the explosion, and iodine and nitrogen are set free. According to the experiments of M. Colin, iodide of nitrogen consists of 1 eq. of nitrogen and 3 eq. of iodine.

It is conveniently made, according to Serullas, by saturating alcohol of 0·852 with iodine, adding a large quantity of pure ammonia, and agitating the mixture. On diluting with water, teriodide of nitrogen subsides, which should be washed by repeated affusion of water and decantation. As thus prepared it is very finely divided, and may be pressed under water without detonating; but if, subsequently to its formation, it is put in contact with pure ammonia, it will afterwards detonate with the same facility as that prepared in the usual manner. Water and teriodide of nitrogen mutually decompose each other, giving rise to the formation of hydriodic and iodic acids and ammonia. The change takes place slowly in cold water; but it is completed in a few minutes, and with scarcely any disengagement of nitrogen, when gentle heat is applied. When a little nitric or sulphuric acid is used, ammonia and iodic acid are alone produced. (An. de Ch. et Ph. xlii. 201.)

Its eq. 393·05; symb. $N + 3I$, or NI_3.

Iodides of Phosphorus.—Iodine and phosphorus combine readily in the cold, evolving so much heat as to kindle the phosphorus, if the experiment is made in the open air; but in close vessels no light appears. One of these compounds, apparently a protiodide, is formed of 1 part of phosphorus and 7 or 8 parts of iodine. It has an orange colour, fuses at 212°, sublimes unchanged by heat, and is decomposed by water, with the elements of which it gives rise to hydriodic and phosphorous acids, while phosphorus is set free. Its eq. is 142·0; symb. $P + I$, or PI.

The sesquiodide is formed by the action of 1 part of phosphorus and 12 of iodine. It appears as a dark grey crystalline mass, fusible at 84°, and yields with water hydriodic and phosphorous acids, from which circumstance its elements are supposed to be in the ratio of 2 eq. of phosphorus to 3 eq. of iodine.

Its eq. is 410·3; symb. $2P + 3I$, or P_2I_3.

The periodide is prepared with 1 part of phosphorus and 20 of iodine, and is a black compound, fusible at 114°. As by the action of water it yields hydriodic and phosphoric acids only, it is inferred to contain phosphorus and iodine in the ratio of 2 eq. to 5 eq. Thus,

1 eq. Periodide Phos. and 5 eq. water	yield	1 eq. Phos. Acid. and 5 eq. Hydriodic Acid.
$P_2I_5 + 5HO$.		$P_2O_5 + 5HI$.

Its eq. is 662·9; symb. $2P + 5I$, or P_2I_5.

Iodide of Sulphur.—This compound is formed by heating gently 4 parts of iodine with 1 of sulphur. The product has a dark colour and radiated appearance like antimony. Its elements are easily disunited by heat.

SECTION XIV.

BROMINE.

Bromine was discovered in 1826 by Balard of Montpellier. The name originally applied to it was *muride,* but the term *brome* or *bromine,* from *βρωμος graveolentia,* signifying a strong or rank odour, has since been substituted. (An. of Phil. xviii. 381.)

Bromine in its chemical relations bears a close analogy to chlorine and iodine, and has hitherto been always found in nature associated with the former, and sometimes also with the latter. It exists in sea-water in the form of bromide of sodium or magnesium. Its relative quantity, however, is very minute; and even the uncrystallizable residue called *bittern,* left after chloride of sodium has been separated from sea-water by crystallization, contains it in small proportion. It may apparently be regarded as an essential ingredient of the saline matter of the ocean; for it has been detected in the waters of the Mediterranean, Baltic, North Sea, and Frith of Forth. It has also been found in the waters of the Dead Sea, and in a variety of salt springs in Germany. Daubeny has detected it in several mineral springs in England, and states that it is rarely wanting in those springs which contain much common salt, except that of Droitwich in Worcestershire. Balard found that it exists in marine plants growing on the shores of the Mediterranean, and has procured it in appreciable quantity from the ashes of sea-weeds that furnish iodine. He has likewise detected its presence in the ashes of some animals, especially in those of the *Janthina violacea,* one of the testaceous mollusca.

Prop.—Bromine is usually extracted from bittern, and its mode of preparation is founded on the property which chlorine possesses of decomposing hydrobromic acid, uniting with its hydrogen, and setting bromine at liberty. Accordingly, on adding chlorine to bittern, the free bromine immediately communicates an orange-yellow tint to the liquid; and, on heating the solution to its boiling point, the red vapours of bromine are expelled, and may be condensed by being conducted into a tube surrounded with ice. It was this change of colour produced by chlorine that led to the discovery of bromine. The method recommended by Balard for procuring this substance, as well as for detecting the presence of hydrobromic acid, is to transmit a current of chlorine gas through bittern, and then to agitate a portion of sulphuric ether with the liquid. The ether dissolves the whole of the bromine, from which it receives a beautiful hyacinth-red tint, and on standing it rises to the surface. When the ethereal solution is agitated with caustic potassa its colour entirely disappears, owing to the formation of bromide of potassium and bromate of potassa, the former of which is obtained in cubic crystals by evaporation. The bromine may then be set free by means of chlorine, or still better by sulphuric acid and the peroxide of manganese. The process should be conducted in a retort, the beak dipping into cold water, which collects the bromine driven over by heat. Balard has subsequently improved the process so much, that it is now produced in considerable quantity, and sold in Paris as an article of commerce.

Prop.—At common temperatures bromine is a liquid, the colour of which is blackish-red when viewed in mass and by reflected light, but appears hyacinth-red when a thin stratum is interposed between the light and the observer. Its odour, which somewhat resembles that of chlorine, is very disagreeable, and its taste powerful. Its sp. gr. is about 3. By a temperature between zero and $-4°$ it is congealed, and in that state is brittle. Its volatility is considerable; for at common temperatures it emits red-coloured vapours, which are very similar in appearance to those of nitrous acid; and at 116·5° it enters into ebullition. The sp. gr. of its vapour was found by Mitscherlich to be 5·54, and the number calculated from its equivalent is 5·3930: 100 cubic inches at 60° and 30 inches B. should weigh 167·25 grains. It is a non-conductor of electricity, and undergoes no chemical change whatever from the agency of the imponderables. It may be transmitted through a red-hot glass tube, and be exposed to the agency of galvanism, without evincing the least trace of decomposition. Like oxygen, chlorine, and iodine, it is a negative electric. It is soluble in water, alcohol, and ether, the latter being its best solvent. It does not redden litmus paper, but bleaches it rapidly like chlorine; and it likewise discharges the blue colour from a solution of indigo. Its vapour extinguishes a lighted taper; but, before going out, the taper burns for a few seconds with a flame which is green at its base and red at its upper part. Some inflammable substances take fire by contact with bromine, in the same manner as when introduced into an atmosphere of chlorine. It acts with energy on organic matters, such as wood or cork, and corrodes the animal texture; but, if applied to the skin for a short time only, it communicates a yellow stain, which is less intense than that produced by iodine, and soon disappears. To animal life it is highly destructive, one drop of it placed on the beak of a bird having proved fatal.

From the close resemblance observable between chlorine and bromine, Balard was of course led to examine its relations with hydrogen, and found that these substances may readily be made to unite; the product of the combination being a gas very similar to hydrochloric and hydriodic acid gases, whence it has received the name of *hydrobromic* acid gas. In its action on metals, also, bromine presents the closest similarity to that which chlorine exerts on the same substances. Antimony and tin take fire by contact with bromine; and its union with potassium is attended with such intense heat as to cause a vivid flash of light, and often to burst the vessel in which the experiment is performed. It affinity for metallic oxides is feeble. By the action of alkalies and water it is resolved into hydrobromic and bromic acids, suffering the same kind of change as chlorine or iodine when similarly treated.

According to all the experiments hitherto made, bromine appears to be an element. It is so very similar in most aspects to chlorine and iodine, and in the order of its chemical relations is so constantly intermediate between them, that Balard at first supposed it to be some unknown compound of these substances. There seems, however, to be no good ground for the supposition; but, on the contrary, an experiment performed by De la Rive affords a very strong argument against it. He finds that when a compound of bromine and iodine is mixed with starch, and exposed to the influence of galvanism, bromine appears at the + and iodine at the − wire, where the starch acquires a blue tint. On making the experiment with bromine containing a little bromide of iodine, the same appearance ensues; but if iodine is not previously added, the starch does not receive a tint of blue.

Bromine is in most cases easily detected by means of chlorine; for this substance displaces bromine from its combination with hydrogen, metals, and most other bodies. The appearance of its vapour or the colour of its solution in ether will then render its presence obvious. Like chlorine, it forms a crystalline hydrate when exposed to 32° F. in contact with water. The crystals are octohedral, of a beautiful red tint, and suffer decomposition at 54°. (Löwig.)

Berzelius determined the equivalent of bromine in the same way as that of iodine, namely, by heating a known weight of bromide of silver in a current of chlorine gas, so as to displace the bromine, and obtain chloride of silver.

Its eq. is 78·4; eq. vol. = 100; symb. Br.

The compounds of bromine described in this section are as follows:—

	Bromine.		Equiv.		Formulæ.
Hydrobromic Acid .	78·4	1 eq. + Hydrogen	1	1 eq. = 79·4	HBr.
Bromic Acid .	78·4	1 eq. + Oxygen	40	5 eq. = 118·4	BrO_5.

	Bromine.	Equiv.	Formulæ.
Chloride of Bromine .	Composition uncertain.		
Bromides of Iodine .	Composition uncertain.		
Bromide of Sulphur .	Composition uncertain.		
Protobromide of Phosp.	78·4 1 eq. + Phosph.	15·7 1 eq. = 94·1	PBr.
Perbromide of Phos.	. 392 5 eq. + do.	31·4 2 eq. = 423·4	P_2Br_5.
Bromide of Carbon .	Composition uncertain.		
Terbromide of Silicon	. 235·2 3 eq. + Silicon	22·5 1 eq. = 257·7	$SiBr_3$.

Hydrobromic Acid.—Prep.—No chemical action takes place between the vapour of bromine and hydrogen gas at common temperatures, not even by the agency of the direct solar rays; but, on introducing a lighted candle, or a piece of red-hot iron, into the mixture, combination ensues in the vicinity of the heated body, though without extending to the whole mixture, and without explosion. The combination is readily effected by the action of bromine on some of the gaseous compounds of hydrogen. Thus, on mixing the vapour of bromine with hydriodic acid, hydrosulphuric acid, or phosphuretted hydrogen gases, decomposition ensues, and hydrobromic acid gas is generated. It may be conveniently made for experimental purposes by a process similar to that for forming hydriodic acid. A mixture of bromine and phosphorus, slightly moistened, yields, by the aid of gentle heat, a large quantity of pure hydrobromic acid gas, which should be collected either in dry glass bottles, or over mercury.

Prop.—It is a colourless gas, has an acid taste, and pungent odour. It irritates the glottis powerfully, so as to excite cough, and when mixed with moist air, yields white vapours, which are denser than those occasioned under the same circumstances by hydrochloric acid gas. It undergoes no decomposition when transmitted through a red-hot tube, either alone or mixed with oxygen. It is not affected by iodine; but chlorine decomposes it instantly, with production of hydrochloric acid gas, and deposition of bromine. It may be preserved without change over mercury; but potassium and tin decompose it with facility, the former at common temperatures, and the latter by the aid of heat. It is very soluble in water. The aqueous solution may be made by treating bromine with hydrosulphuric acid dissolved in water, or, still better, by transmitting a current of hydrobromic acid gas into pure water. The liquid becomes hot during the condensation, acquires great density, increases in volume, and emits white fumes when exposed to the air. This acid solution is colourless when pure, but possesses the property of dissolving a large quantity of bromine, and then receives the tint of that substance.

Chlorine decomposes the solution of hydrobromic acid in an instant. Nitric acid likewise acts upon it, though less suddenly, occasioning the disengagement of bromine, and probably the formation of water and nitrous acid. Nitro-hydrobromic acid is analogous to *aqua regia*, and possesses the property of dissolving gold. The elements of sulphuric and hydrobromic acids react on each other in a slight degree; and hence, on decomposing bromide of potassium by sulphuric acid, the hydrobromic is generally mixed with a little sulphurous acid gas.

The composition of hydrobromic acid gas is easily inferred from the two following facts. 1. On decomposing hydrobromic acid gas by potassium, a quantity of hydrogen remains, precisely equal to half the volume of the gas employed; and, 2, when hydriodic acid gas is decomposed by bromine, the resulting hydrobromic acid occupies the very same space as the gas which is decomposed. Hence hydrobromic is analogous to hydriodic and hydrochloric acid gases in containing equal measures of bromine vapour and hydrogen gas united without any change of volume; and since

			Grains.
50	cubic inches of	Bromine Vapour weigh	83·6400
50	do.	Hydrogen Gas	1·0684
100	do.	Hydrobromic Acid must weigh . . .	84·7084

These numbers are in the ratio of 1 to 78·4, which is the composition of the gas by weight. Its sp. gr. is 2·731.

Since bromine decomposes hydriodic, and chlorine hydrobromic acid, bromine, in relation to hydrogen, is intermediate between chlorine and iodine; for it has a stronger affinity for hydrogen than iodine, and a weaker than chlorine. The affinity of bromine and oxygen for hydrogen appears nearly similar; for while oxygen cannot detach hydrogen from bromine, bromine does not decompose watery vapour.

The salts which hydrobromic forms with alkalies are bromides of the metals. Like the free acid, they are decomposed, and the presence of bromine is detected by means of chlorine. On mixing a soluble bromide with the nitrates of the protoxides of lead, silver, and mercury, white precipitates are obtained, which are very similar in appearance to the chlorides of those metals, but which are metallic bromides. On the addition of chlorine, the vapour of bromine is evolved.

Its eq. is 79·4; eq. vol. $= 200$; symb. $H + Br$, or HBr.

Bromic Acid.—Prep.—The only compound yet known of bromine and oxygen is that formed by the action of bromine on potassa, when a change exactly similar to that produced by chlorine ensues, whereby bromide of potassium and bromate of potassa are generated; and the latter, being much less soluble than the former, is readily separated by evaporation. The bromates of the other alkalies and alkaline earths may be prepared in a similar manner.

The acid may be procured in a separate state by decomposing a dilute solution of bromate of baryta with sulphuric acid, so as to precipitate the whole of the baryta. The resulting solution of bromic acid may be concentrated by slow evaporation until it acquire the consistence of syrup; but on raising the temperature, in order to expel all the water, one part of the acid is volatilized, and the other resolved into oxygen and bromine. A similar result took place when the evaporation was conducted *in vacuo* with sulphuric acid; and accordingly all attempts to procure anhydrous bromic acid have hitherto failed.

Prop.—Bromic acid has scarcely any odour, but its taste is very acid, though not at all corrosive. It reddens litmus paper powerfully at first, and soon after destroys its colour. It is not affected by nitric or sulphuric acids except when the latter is highly concentrated, in which case bromine is set free, and effervescence, probably owing to the escape of oxygen gas, ensues. From the analysis of bromate of potassa, bromic acid is obviously similar in constitution to iodic, chloric, and nitric acids; that is, it consists of one equivalent of bromine united with five of oxygen. Its salts are analogous to the chlorates and iodates. Thus, bromate of potassa is converted by heat into bromide of potassium, with disengagement of pure oxygen gas, deflagrates like nitre when thrown on burning charcoal, and forms with sulphur a mixture which detonates by percussion. The acid of the bromates is decomposed by deoxidizing agents, such as sulphurous and hydrosulphuric acids, in the same manner as the acid of the iodates. The bromates likewise suffer decomposition from the action of hydrobromic and hydrochloric acids.

Bromate of potassa is said not to precipitate the salts of lead, but to occasion a white precipitate with nitrate of silver, and a yellowish-white with protonitrate of mercury; characters which, if true, serve as a good test to distinguish bromate from iodate and chlorate of potassa.

Its eq. is 118·4; symb. $\mathrm{Br} + 5\mathrm{O}$,$\overset{\cdot\overset{\cdot\ \cdot}{}\cdot\ \cdot}{\mathrm{Br}}$, or BrO_5.

Chloride of Bromine.—This compound may be formed at common temperatures by transmitting a current of chlorine through bromine, and condensing the disengaged vapours by means of a freezing mixture. The resulting chloride is a volatile fluid of a reddish-yellow colour, much less intense than that of bromine; its odour is penetrating, and causes a discharge of tears from the eyes; and its taste very disagreeable. Its vapour is a deep yellow, like chlorous acid, and it enables metals to burn as in an atmosphere of chlorine, doubtless giving rise to the formation of metallic chlorides and bromides.

Chloride of bromine is soluble in water without decomposition; for the solution possesses the colour, odour, and bleaching properties of the compound, and discharges the colour of litmus paper without previously reddening it. By the action of the alkalies it is decomposed, being converted, by means of the elements of water, into hydrochloric and bromic acids.

Bromide of Iodine.—These substances act readily on each other, and appear capable of uniting in two proportions. The protobromide is a solid, convertible by heat into a reddish-brown vapour, which in cooling condenses into crystals of the same colour, and of a form resembling that of fern leaves. An additional quantity of bromine converts these crystals into a fluid, which in appearance is like a strong solution of iodine in hydriodic acid. This compound dissolves without decomposition in water, but with the alkalies yields hydrobromic and iodic acids. The existence of two bromides of iodine can scarcely be regarded as satisfactorily established.

Bromide of Sulphur.—On pouring bromine on sublimed sulphur, combination ensues, and a fluid of an oily appearance and reddish tint is generated. In odour it somewhat resembles chloride of sulphur, and like that compound emits white vapours when exposed to the air; but its colour is deeper. It reddens litmus paper faintly when dry, but strongly if water is added. Cold water acts slowly upon bromide of sulphur; but at a boiling temperature the action is so violent that a slight detonation occurs, and three compounds, hydrobromic, hydrosulphuric, and sulphuric acids are formed. The formation of these substances is of course attributable to decomposition of water, and the union of its elements with bromine and sulphur. Bromide of sulphur is likewise decomposed by chlorine, which unites with sulphur, and displaces bromine.

The composition of bromide of sulphur is unknown. It dissolves an excess both of chlorine and sulphur, and its elements separate from each other so readily, that it has hitherto been impracticable to procure a definite compound.

Bromide of Phosphorus.—When bromine and phosphorus are brought into contact in a flask filled with carbonic acid gas, they act suddenly on each other with evolution of heat and light, and two compounds are generated: one, a crystalline solid, which is sublimed and collects in the upper part of the flask; and the other, a fluid, which remains at the bottom. The former contains the most bromine, and the latter is supposed by Balard to consist of single equivalents of its elements.

The protobromide retains its liquid from even at 52° F. It is readily converted into vapour by heat, and on exposure to the air emits penetrating fumes. It reddens litmus paper faintly, an effect which is probably owing to the presence of moisture. With water it acts energetically and with free disengagement of heat, hydrobromic acid gas being evolved when only a few drops of water are employed; but if a large quantity is used, the gas is dissolved, and the acid solution leaves by evaporation a residuum, which burns slightly when dried, and is converted into phosphoric acid.

The perbromide is yellow in its solid state; but with gentle heat it becomes a red-coloured liquid, which by increase of temperature is converted into a vapour of the same tint. On cooling after fusion it yields rhombic crystals; but when its vapour is condensed, the crystals are acicular. It is decomposed by metals, probably with the formation of metallic bromides and phosphurets. It emits dense penetrating fumes on exposure to the air, and with water gives rise to the production of hydrobromic and phosphoric acids. Hence its elements should be in the ratio of 2 eqs. of phosphorus to 5 eqs. of bromine.

Chlorine has a greater affinity for phosphorus than bromine, and decomposes both the bromides with evolution of the vapour of bromine. These compounds are not decomposed by iodine; but, on the contrary, bromine decomposes iodide of phosphorus.

Terbromide of Silicon.—This compound was made by Serullas in precisely the same mode as that described for forming the terchloride. When purified from free bromine by mercury, and re-distilled, it is a colourless liquid, which emits dense vapours in an open vessel, being decomposed by the moisture of the air, and is denser than strong sulphuric acid. At 302° it enters into ebullition, and freezes at 10°. Potassium, when gently heated, acts on it with such energy that detonation ensues. By water it is resolved into hydrobromic and silicic acids. (Phil. Mag. and Annals, xi. 295.)

Its eq. is 257·7; symb. $Si + 3Br$, or $SiBr_3$.

SECTION XV.

FLUORINE.

The substance to which this name is applied, though long known to exist in various compounds, has only recently been obtained in an insulated form, and therefore the properties peculiar to it in that state are but imperfectly known. It was first procured by Baudrimont by passing fluoride of boron over minium heated to redness, and receiving the gas in a dry vessel. As it is mixed with a large quantity of oxygen, his present method is to treat a mixture of fluoride of calcium and peroxide of manganese with strong sulphuric acid. This process, however, does not give a pure gas, as hydrofluoric and fluosilicic acid gases are at the same time evolved. The presence of the latter does not prevent the observation of some of the properties of fluorine. It is a gas of a yellowish-brown colour; its odour resembles chlorine and burnt sugar; it bleaches. It does not act on glass, but combines directly with gold. (Phil. Mag. x. 149.) The latter fact is confirmed by the observations of Messrs. Knox, who have succeeded so far in the preparation of fluorine as to leave no doubt of its existence as a coloured gas. (Phil. Mag. x. 107.) Its sp. gr. is 1·289. From the nature of its compounds it appears to belong to the class of negative electrics, and, like oxygen and chlorine, to have a powerful affinity for hydrogen and metallic substances. Berzelius determined its eq. by finding that 100 parts of pure fluoride of calcium yield with sulphuric acid 175 parts of sulphate of lime.

Its eq. is 18·68; eq. vol. = 100; symb. F.

The compounds of fluorine described in this section are the following:—

	Fluorine.			Equiv.	Formulæ.
Hydrofluoric Acid .	18·68 1 eq.	+ Hydrogen	1	1 eq. = 19·68	HF.
Fluoboric Acid .	56·08 3 eq.	+ Boron	10·9	1 eq. = 66·98	BF_3.
Fluosilicic Acid .	56·08 3 eq.	+ Silicon	22·5	1 eq. = 78·58	SiF_3.

Hydrofluoric Acid.—Hist. and Prep.—This acid was first procured in its pure state in the year 1810 by Gay-Lussac and Thenard, and described in the second volume of their *Recherches Physico-Chimiques.* It is prepared by acting on the mineral called *fluor-spar*, which is a fluoride of calcium, carefully separated from siliceous earth and reduced to fine powder, with twice its weight of concentrated sulphuric acid. The mixture is made in a leaden retort; and, on applying heat, an acid and highly corrosive vapour distils over, which must be collected in a receiver of the same metal surrounded with ice. As the materials swell up considerably during the process, owing to a quantity of vapour forcing its way through a viscid mass, the retort should be capacious. At the close of the operation pure hydrofluoric acid is found in the receiver, and the retort contains dry sulphate of lime. The chemical changes are precisely the same as in the formation of hydrochloric acid gas, fluorine being substituted for chlorine and calcium for sodium. If the oil of vitriol is of sufficient strength, all its water is decomposed, and the resulting hydrofluoric acid is anhydrous.

Prop.—It is at 32° a colourless fluid, and remains in that state at 59°, if preserved in well-stopped bottles; but, when exposed to the air, it flies off in dense white fumes, which consist of the acid vapour combined with the moisture of the atmosphere. Its sp. gr. is 1·0609; but its density may be increased to 1·25 by gradual additions of water

Its affinity for this liquid far exceeds that of the strongest sulphuric acid, and the combination is accompanied with a hissing noise, as when red-hot iron is quenched by immersion in water.

Its vapour is much more pungent than chlorine or any of the irritating gases. Of all known substances it is the most destructive to animal matter. When a drop of the concentrated acid, of the size of a pin's head, comes in contact with the skin, instantaneous disorganization ensues, and deep ulceration of a malignant character is produced. On this account the greatest care is requisite in its preparation. It acts energetically on glass. The transparency of the glass is instantly destroyed, heat is evolved, and the acid boils, and in a short time entirely disappears. A colourless gas, commonly known by the name of *fluo-silicic acid gas*, is the sole product. This compound is always formed when hydrofluoric acid comes in contact with a siliceous substance. For this reason it cannot be preserved in glass; but must be prepared and kept in metallic vessels. Those of lead, from their cheapness, are often used; but vessels of silver or platinum are preferable. In consequence of its powerful affinity for siliceous matter, hydrofluoric acid may be employed for etching on glass; and when used with this intention, it should be diluted with three or four times its weight of water.

Hydrofluoric acid has all the usual characters of a powerful acid. It has a strong sour taste, reddens litmus paper, and neutralizes alkalies, either forming salts termed *hydrofluates*, or most generally giving rise to metallic fluorides. All these compounds are decomposed by strong sulphuric acid with the aid of heat, and the hydrofluoric acid while escaping may be detected by its action on glass.

On some of the metals it acts violently, especially on the bases of the alkalies. Thus, when potassium is brought in contact with the concentrated acid, an explosion attended with heat and light ensues; hydrogen gas is disengaged, and a white compound, fluoride of potassium, is generated. It is a solvent for some elementary principles which resist the action even of nitro-hydrochloric acid. Thus, it dissolves silicon, zirconium, and columbium, with evolution of hydrogen gas; and, when mixed with nitric acid, it proves a solvent for silicon which has been condensed by heat, and for titanium. Nitro-hydrofluoric acid, however, is incapable of dissolving gold and platinum. Several oxidized bodies, which are not attacked by sulphuric, nitric, or hydrochloric acid, are readily dissolved by hydrofluoric acid. As examples of this fact, several of the weaker acids, such as silica or silicic acid, titanic, columbic, molybdic, and tungstic acids may be enumerated. (Berzelius.)

A different view of the compounds of fluorine was originally taken by Gay-Lussac and Thenard, and is still held by some chemists. They adopted the opinion that hydrofluoric acid is a compound of a certain inflammable principle and oxygen, and applied to it the name of *fluoric acid*, previously introduced by Scheele. Fluor-spar, on this view, is a fluate of lime; and when this salt is decomposed by oil of vitriol, the fluoric is merely displaced by the sulphuric acid, and the former passes off, combined with the water of the latter. What I have described as anhydrous hydrofluoric acid is, according to this hypothesis, hydrated fluoric acid; and, when acted upon by potassium, this metal is oxidized at the expense of the water, and the potassa thus generated unites with fluoric acid, forming, not fluoride of potassium, but fluate of potassa. The equivalent of fluoric acid, as inferred from the analysis of Berzelius, is 10·68; for 39·18 parts or one equivalent of fluor-spar is supposed to contain 28·5 parts of lime (20·5 calcium and 8 oxygen), thus leaving 10·68 as the equivalent of the acid.

The theory, according to which fluor-spar is a compound of fluorine and calcium, originated as a suggestion with M. Ampère of Paris, and was afterwards supported experimentally by Davy. It was found that pure hydrofluoric acid evinces no sign of containing either oxygen or water. Charcoal may be intensely heated in the vapour of the acid without the production of carbonic acid. When hydrofluoric acid was neutralized with dry ammoniacal gas, a white salt resulted, from which no water could be separated; and on treating this salt with potassium, no evidence could be obtained of the presence of oxygen. On exposing the acid to the agency of galvanism, there was a disengagement at the negative pole of a small quantity of gas, which from its combustibility was inferred to be hydrogen; while the platinum wire of the opposite side of the battery was rapidly corroded, and became covered with a chocolate-coloured powder. Davy explained these phenomena by supposing that hydrofluoric acid was resolved into its elements; and that fluorine, at the moment of arriving at the positive side of the battery, entered into combination with the platinum wire which was employed as a conductor. Unfortunately, however, he did not succeed in obtaining fluorine in an insulated state. Indeed, from the noxious vapours that arose during the experiment, it was impossible to watch its progress, and examine the different products with that precision which is essential to the success of minute chemical inquiries, and which Davy has so frequently displayed on other occasions.

Though these researches led to no conclusive result, they afforded so strong a presumption in favour of the opinion of Ampère and Davy, that it was adopted by several other chemists. This view has received strong additional support from the experiments of M. Kuhlman. (Quarterly Journal of Science for July, 1827, p. 205.) It was found by this chemist that fluor-spar is not in the slightest degree decomposed by the action of anhydrous sulphuric acid, whether at common temperatures or at a red heat. The experiment was made both by transmitting the vapour of anhydrous sulphuric acid over fluor-spar heated to redness in a tube of platinum, and by putting the mineral into the liquid acid. In neither case did decomposition ensue; but, when the former experiment was repeated, with the difference of employing concentrated hydrous instead of anyhdrous sulphuric acid, evolution of hydrofluoric acid was produced. M. Kuhlman also transmitted hydrochloric acid gas over fluor-spar at a red heat, when hydrofluoric acid was disengaged, without any evolution of hydrogen, and chloride of calcium remained. I am aware of no satisfactory explanation of these facts, except by regarding fluor-spar as a compound of fluorine and calcium, and hydrofluoric acid as a compound of fluorine and hydrogen. I shall accordingly adopt this view in the subsequent pages, and never employ the term fluoric acid except when explaining phenomena according to the theory of Gay-Lussac.

Its eq. is 19·68; symb. $H + F$, or HF.

Fluoboric Acid.—Prep.—The chief difficulty in determining the nature of hydrofluoric acid arises from the water of the sulphuric acid which is employed in its preparation. To avoid this source of uncertainty, Gay-Lussac and Thenard made a mixture of vitrified boracic acid and fluor-spar, and exposed it in a leaden retort to heat, under the expectation that as no water was present, anhydrous fluoric acid would be obtained. In this, however, they were disappointed; but a new gas came over, to which they applied the term of *fluoboric acid gas*. A similar train of reasoning led Davy about the same time to the same discovery; though the French chemists had the advantage in priority of publication. Another process given by Dr. Davy, is to mix 1 part of vitrified boracic acid and 2 of fluor-spar with 12 parts of strong sulphuric acid, heating the mixture gently in a glass flask (Phil. Trans., 1812); but the gas thus developed contains a considerable quantity of fluosilicic acid. Fluoboric acid gas may also be formed by heating a strong solution of hydrofluoric and boracic acids in a metallic retort.

In the decomposition of fluor-spar by vitrified boracic acid, the former and part of the latter undergo an interchange of elements. The fluorine uniting with boron gives rise to fluoboric acid gas; and by the union of calcium and oxygen lime is generated, which combines with boracic acid, and is left in the retort as borate of lime. Fluoboric acid gas, therefore, is composed of boron and fluorine. Those who adopt the theory of Gay-Lussac give a different explanation, and regard this gas as a compound of fluoric and boracic acids. The lime of fluor-spar is supposed to unite with one portion of boracic acid, and fluoric acid at the moment of separation with another, yielding borate of lime and fluoboric acid gas.

Prop.—It is a colourless gas, has a penetrating pungent odour, and extinguishes flame on the instant. Its sp. gr. according to Thomson, is 2·3622. It reddens litmus paper as powerfully as sulphuric acid, and forms salts with alkalies which are called *fluoborates.* It has a singularly great affinity for water. When mixed with air or any gas which contains watery vapour, a dense white cloud, a combination of water and fluoboric acid, appears, thus affording an extremely delicate test of the presence of moisture in gases. Water acts powerfully on this gas, absorbing, according to Dr. Davy, 700 times its volume, during which the water increases in temperature and volume. The solution is limpid, fuming, and very caustic. On the application of heat, part of the gas is disengaged; but afterwards the whole solution is distilled.

Gay-Lussac and Thenard and Dr. Davy were of opinion that fluoboric acid gas is dissolved by water without decomposition; but Berzelius denies the accuracy of their observation. On transmitting the gas into water until the liquid acquires a sharply sour taste, but is far from being saturated, a white powder begins to subside; and, on cooling, a considerable quantity of boracic acid is deposited in crystals. It appears that in a certain state of dilution, part of the fluoboric acid and water mutually decompose each other, with formation of boracic and hydrofluoric acids. The latter unites, according to Berzelius, with undecomposed fluoboric acid, forming what he has called *boro-hydrofluoric acid.* On concentrating the liquid by evaporation, the boracic and hydrofluoric acids decompose each other, and the original compound is reproduced.

Fluoboric acid gas does not act on glass, but attacks animal and vegetable matters with energy, converting them like sulphuric acid into a carbonaceous substance. This action is most probably owing to its affinity for water.

When potassium is heated in fluoboric acid gas, the metal takes fire, and a chocolate-coloured solid, wholly devoid of metallic lustre, is formed. This substance is a mixture of boron and fluoride of potassium, from which the latter is dissolved by water, and the boron is left in a solid state.

The composition of fluoboric acid gas has not hitherto been determined by direct experiment. Dr. Davy ascertained that it unites with an equal measure of ammoniacal gas, forming a solid salt; and that it also combines with twice and three times its volume of ammonia, yielding liquid compounds. In the former salt the relative weights of the constituent gases are in the ratio of their specific gravities; and if the compound consists of one equivalent of each, it will be constituted of

Fluoboric Acid Gas	2·3622	68·04	1 eq.
Ammoniacal Gas	0·5898	17	1 eq.

so that the equivalent of the acid may be assumed in round numbers to be 68. Now supposing this acid to be formed of 3 eqs. of fluorine and one of boron, its eq. will be 64·04, a number which approximates to the preceding. This view is consistent with the composition of boracic acid as formerly given, and with the conversion of fluoboric acid by water into hydrofluoric and boracic acids.

Its symb. is $B + 3F$, or BF_3.

Fluosilicic Acid.—*Prep.*—This gas is formed whenever hydrofluoric and silicic acids come in contact; and hence pure hydrofluoric acid can be prepared in metallic vessels only, and with fluor-spar that is free from rock crystal. The most convenient method of procuring it is to mix in a retort one part of pulverized fluor-spar with its own weight of sand or pounded glass, and two parts of strong sulphuric acid. On applying a gentle heat, fluosilicic acid gas is disengaged with effervescence, and may be collected over mercury.

The chemical changes attending this process are differently explained, according to the view which is taken concerning the nature of the product. In regarding fluor-spar as a compound of fluoric acid and lime, the former at the moment of being set free is thought to unite directly with silicic acid, thereby giving rise to a compound of silicic and fluoric acids. But, for reasons already stated, fluor-spar is not considered as fluate of lime; and therefore this view cannot be admitted. It is inferred, on the contrary, that when, by the action of sulphuric acid on fluoride of calcium, hydrofluoric acid is generated, the elements of this acid react on those of silicic acid, and give rise to the production of water and fluosilicic acid gas. This gas is therefore a fluoride of silicon. It may occur to some whether hydrofluoric acid does not unite directly with silicic acid; but this idea is inconsistent with the proportion in which the elements of the gas are found to be united.

Prop.—It is a colourless gas, which extinguishes flame, destroys animals that are immersed in it, and irritates the respiratory organs powerfully. It does not corrode glass vessels provided they are quite dry. When mixed with atmospheric air it forms a white cloud, owing to the presence of watery vapour. Its sp. gr., according to Thomson, is 3·6111; and 100 cubic inches of it at 60°, and when the barometer stands at 30 inches, weigh 111·985 grains.

Water acts powerfully on fluosilicic acid gas, of which it condenses, according to Dr. Davy, 365 times its volume. (Phil. Trans. for 1812.) The gas suffers decomposition at the moment of contact with water, silicic acid in the form of a gelatinous hydrate being deposited, which when well washed is quite pure. The liquid, which has a sour taste and reddens litmus paper, contains the whole of the hydrofluoric acid, together with two-thirds of the silicic acid which was originally present in the gas. (Berzelius.) By conducting fluosilicic acid gas into a solution of ammonia, complete decomposition ensues:—hydrofluoric acid unites with the alkali, forming hydrofluate of ammonia, and all the silicic acid is deposited. On this fact is founded the mode of analyzing fluosilicic acid gas adopted by Dr. Davy and Thomson.

The solution which is formed by fully saturating water with fluosilicic acid gas is powerfully acid, and emits fumes on exposure to the air. It is commonly known by the name of *silicated fluoric acid;* but a more appropriate term is *silico-hydrofluoric acid.* According to the experiments of Berzelius, it appears to be a definite compound of hydrofluoric and silicic acids, in the ratio of 3 eqs. of the former to 2 of the latter. If evaporated before separation from the silicic acid deposited by the action of water on fluosilicic acid gas, this compound is reproduced. But if the solution is poured off from the silicic acid thus deposited, and then evaporated, fluosilicic acid gas is at first evolved, and subsequently hydrofluoric acid and water are expelled. The evaporation of silico-hydrofluoric acid *in vacuo* is attended by a similar change, so that this acid cannot be obtained free from water. It does not corrode glass; but, when evaporated in glass vessels, the production of free hydrofluoric acid of course gives rise to corrosion.

On neutralizing silico-hydrofluoric acid with ammonia, and gently evaporating to dryness, all the silicic acid is rendered insoluble. By exactly neutralizing with carbonate of potassa, a sparingly soluble double fluoride of silicon and potassium subsides: the precipitation is still more complete with chloride of barium, when the insoluble fluoride of silicon and barium is generated. A variety of similar compounds may be obtained either by double decomposition, or by the action of silico-hydrofluoric acid on metallic oxides.

Its eq. is 78·58; symb. $Si + 3F$, or SiF_3.

ON THE COMPOUNDS OF THE SIMPLE NON-METALLIC ACIDIFIABLE COMBUSTIBLES WITH EACH OTHER.

SECTION I.

HYDROGEN AND NITROGEN.—AMMONIACAL GAS.

Hist. and Prep.—The aqueous solution of ammonia, under the name of *spirit of hartshorn*, has been long known to chemists; but its existence as a gas was first noticed by Priestley, who described it in his works under the title of *alkaline air*. It is often called the *volatile alkali;* but the terms ammonia and ammoniacal gas are now usually employed. Although a product of the decomposition of organic substances, it has been thought better to describe it here, from its great importance in inorganic chemistry.

An abundant supply of ammoniacal gas may be obtained from any salt of ammonia by the action of a pure alkali or alkaline earth; but hydrochlorate of ammonia and lime, from economical considerations, are always employed. The proportions to which I give the preference are equal parts of hydrochlorate of ammonia and well-burned quicklime, considerable excess of lime being taken, in order to decompose the hydrochlorate more expeditiously and completely. The lime is slaked by the addition of water; and as soon as it has fallen into powder, it should be placed in an earthen pan and be covered till it is quite cold, in order to protect it from the carbonic acid of the air. It is then mixed in a mortar with the hydrochlorate of ammonia, previously reduced to a fine powder; and the mixture is put into a retort or other convenient glass vessel. Heat is then applied, and the temperature gradually increased as long as free evolution of gas continues. The residue consists of chloride of calcium and lime.

The gas, thus liberated, must be collected over mercury, as it is most rapidly absorbed by water. Advantage is taken of this property to prepare what is commonly though incorrectly termed liquid ammonia. For this purpose a current of gas is transmitted into distilled water, which is kept cool by means of ice or moist cloths, and the process is continued as long as any gas is absorbed. A highly concentrated solution of ammonia is thus obtained. The most convenient method of preparing ammoniacal gas for purposes of experiment is by applying a gentle heat to the concentrated solution, contained in a glass vessel.

It soon enters into ebullition, and a large quantity of pure ammonia is disengaged.

Prop.—Ammonia is a colourless gas, which has a strong pungent odour, and acts powerfully on the eyes and nose. It is quite irrespirable in its pure form; but when diluted with air it may be taken into the lungs with safety. Burning bodies are extinguished by it, nor is the gas inflamed by their approach. Ammonia, however, is inflammable in a low degree; for, when a lighted candle is immersed in it the flame is somewhat enlarged, and tinged of a pale yellow colour at the moment of being extinguished; and a small jet of the gas will burn in an atmosphere of oxygen. A mixture of ammoniacal and oxygen gases detonates by the electric spark; water being formed, and nitrogen set free. A little nitric acid is generated at the same time, except when a smaller quantity of oxygen is employed than is sufficient for combining with all the hydrogen of the ammonia. (Henry, Phil. Trans., 1809.)

Ammoniacal gas at the temperature of 50° and under a pressure equal to 6·5 atmospheres, becomes a transparent colourless liquid. It is also liquefied, according to Guyton-Morveau, under the common pressure, by a cold of $-70°$; but there is no doubt that the liquid which he obtained was a solution of ammonia in water.

It has all the properties of an alkali in a very marked manner. Thus it has an acrid taste, and gives a brown stain to turmeric paper; though the yellow colour soon re-appears on exposure to the air, owing to the volatility of the alkali. It combines also with acids, and neutralizes their properties completely. All these salts suffer decomposition by being heated with the fixed alkalies or alkaline earths, such as potassa or lime, the union of which with the acid of the salt causes the separation of its ammonia. None of the ammoniacal salts can sustain a red heat without being dissipated in vapour or decomposed,—a character which manifestly arises from the volatile nature of the alkali. If combined with a volatile acid, such as the hydrochloric, the compound itself sublimes unchanged by heat; but when united with an acid which is fixed at a low red heat, such as the phosphoric, the ammonia alone is expelled. It is here considered that the salts of ammonia are formed by its direct union with acids. Another, and a very scientific view, has been adopted by Berzelius. When an electric current is passed through a weak solution of ammonia, it is decomposed by the secondary action, hydrogen from decomposed water being evolved at the negative electrode, and nitrogen at the positive. (Faraday, Phil. Trans., 1834.) But if a portion of mercury form the negative electrode no hydrogen is evolved, and the mercury is rapidly converted into a light porous substance, which has the lustre and all the characters of an amalgam. As soon as it is removed from the influence of the electric current, rapid decomposition ensues, mercury is reproduced, and hydrogen and ammoniacal gases are evolved in the ratio of one measure of the former to two of the latter, according to the observations of Gay-Lussac and Thenard. The production of this compound is explained by Berzelius on the supposition that ammonia, by uniting with an additional eq. of hydrogen, forms a compound which has all the properties of a metal; he therefore calls it ammonium. The oxide of ammonium, the composition of which is represented by the formula $NH_4 + O$, he considers to be the base of the ammoniacal salts. This view is supported by several facts, which will be considered when treating of the salts.

Hydrogen and nitrogen gases do not unite directly, and therefore chemists have no synthetic proof of the constitution of ammonia. Its composition, however, has been determined analytically with great exactness. When a succession of electric sparks is passed through ammoniacal gas, it is resolved into its elements; and the same effect is produced by conducting it through porcelain tubes heated to redness. A. Berthollet analyzed ammonia in both ways, and ascertained that 200 measures of that gas, on being decomposed, occupy the space of 400 measures, 300 of which are hydrogen, and 100 nitrogen. Henry has made an analysis of ammonia by means of electricity, and his experiment proves beyond a doubt that the proportions above given are rigidly exact. (Annals of Philosophy, xxiv. 346.)

	Grains.
Now since 150 cubic inches of Hydrogen weigh	3·205
and 50 of Nitrogen	15·083
100 cubic inches of Ammonia must weigh	18·288

and it is composed by weight of

Hydrogen	3·205	3	or 3 equivalents.
Nitrogen	15·083	14·15	or 1 equivalent.

The sp. gr. of ammonia, according to this calculation, is 0·5898, a number which agrees closely with those ascertained directly by Davy and Thomson.

Ammoniacal gas has a powerful affinity for water. Owing to this attraction, a piece of ice, when introduced into a jar full of ammonia, is instantly liquefied, and the gas disappears in the course of a few seconds. Davy, in his Elements, stated that water at 50°, and when the barometer stands at 29·8 inches, absorbs 670 times its volume of ammonia, and that the solution has a sp. gr. of 0·875. According to Thomson, water at the common temperature and pressure takes up

780 times its bulk. By strong compression, water absorbs the gas in still greater quantity. Heat is evolved during its absorption; and a considerable expansion, independently of the increased temperature, occurs at the same time.

The concentrated solution of ammonia is a clear colourless liquid, of sp. gr. 0·936. It possesses the peculiar pungent odour, taste, alkalinity, and other properties of the gas itself. On account of its great volatility it should be preserved in well-stopped bottles, a measure which is also required to prevent the absorption of carbonic acid. At a temperature of 130° it enters into ebullition, owing to the rapid escape of pure ammonia; but the whole of the gas cannot be expelled by this means, as at last the solution itself evaporates. It freezes at about the same temperature as mercury.

The following table, from Davy's Elements of Chemical Philosophy, shows the quantity of real ammonia contained in 100 parts of solutions of different sp. gravities at 59° F. and when the barometer stands at 30 inches. The sp. gr. of water is supposed to be 10,000.

Table of the Quantity of real Ammonia in Solutions of different Densities.

100 parts of sp. gravity.		Of real Ammonia.	100 parts of sp. gravity.		Of real Ammonia.
8750	contain	32·50	9435	contain	14·53
8875		29·25	9476		13·46
9000		26·00	9513		12·40
9054		25·37	9545		11·56
9166		22·07	9573		10·82
9255		19·54	9597		10·17
9326		17·52	9619		9·60
9385		15·88	9692		9·50

The presence of free ammoniacal gas may always be detected by its odour, by its temporary action on yellow turmeric paper, and by its forming dense white fumes, hydrochlorate of ammonia, when a glass rod moistened with hydrochloric acid is brought near it.

Besides ammonia and ammonium, another compound of nitrogen and hydrogen is believed to exist, the composition of which is represented by the formula NH_2. It is only known in combination, and has been named *Amide.* Its compounds, which are important, will be described in treating of organic chemistry.

The eq. of ammonia is 17·15; eq. vol. = 200; symb. $N + 3H$, or NH_3.

SECTION II.

COMPOUNDS OF HYDROGEN AND CARBON.

Chemists have for several years been acquainted with two distinct compounds of carbon and hydrogen, viz. carburetted hydrogen and olefiant gases; but late researches have enriched the science with several other compounds of a similar nature, to which much interest is attached. They are remarkable for their number, for supplying some instances of isomerism, and for their tendency to unite with and even neutralize powerful acids, without, in their uncombined state, manifesting any ordinary signs of alkalinity. Several of them are particularly distinguished by their chemical affinities; for although compound, they exhibit in their combinations with other substances the characteristics of an element. They have hence been called compound radicals. These compound radicals are closely associated both with the organic and inorganic chemistry. In the latter they must hold a place, as being compounds formed by the direct union of two elements; and in the former they are the roots or radicals of various organic products.

Light Carburetted Hydrogen.—Hist.—This gas is sometimes called *heavy inflammable air*, the *inflammable air of marshes*, and *hydrocarburet.* Agreeably to the principles of chemical nomenclature, taking carbon as the electro-negative element, it is a *dicarburet of hydrogen;* but it is generally termed *light carburetted hydrogen.* It is formed abundantly in stagnant pools during the spontaneous decomposition of dead vegetable matter; and it may readily be procured by stirring the mud at the bottom of them, and collecting the gas, as it escapes, in an inverted glass vessel. In this state it is found to contain 1-20th of carbonic acid gas, which may be removed by means of lime water or a solution of pure potassa, and 1-15th or 1-20th of nitrogen. This is the only convenient method of obtaining it.

Prop.—Colourless, tasteless, nearly inodorous; always gaseous when uncombined; does not change the colour of litmus or turmeric paper. Water, according to Henry, absorbs about 1-60th of its volume. It extinguishes all burning bodies, and is unable to support the respiration of animals. It is highly inflammable; and when a jet of it is set on fire, it burns with a yellow flame, and with a much stronger light than is occasioned by hydrogen gas. With a due proportion of atmospheric air or oxygen gas it forms a mixture which detonates powerfully with the electric spark, or by the contact of flame. The sole products of the explosion are water and carbonic acid.

Dalton first ascertained the real nature of light carburetted hydrogen; and it has since been particularly examined by Thomson, Davy, and Henry. When 100 measures are detonated with rather more than twice their volume of oxygen gas, the whole of the inflammable gas and precisely 200 measures of the oxygen disappear, water is condensed, and 100 measures of carbonic acid are produced. Now, 100 measures of carbonic acid gas contain 100 of carbon vapour and 100 of oxygen gas, just half the oxygen which had been employed; and the remaining oxygen requires 200 measures of hydrogen to form water. Hence, as at 60° F. and 30 inches Bar.,

			Grains.
100	cubic inches of	Carbon Vapour weigh . . .	13·1530
200	do.	Hydrogen Gas	4·2636
100	do.	Light Carburetted Hydrogen must weigh .	17·4166

These weights are obviously in the ratio of 2 to 6·12, as already assigned; and the sp. gr. of such a gas ought to be 0·5594, which is nearly the number found experimentally by Thomson and Henry.

Light carburetted hydrogen is not decomposed by electricity, nor by being passed through red-hot tubes, unless the temperature is very intense, in which case some of the gas does suffer decomposition, each volume yielding two volumes of pure hydrogen gas and a deposit of charcoal. Mixed with chlorine, no action takes place at common temperatures, when quite dry, even if exposed to the direct solar rays. If moist, and the mixture is kept in a dark place, still no action ensues: but if light be admitted, particularly sunshine, decomposition follows. The nature of the products depends upon the proportion of the gases. If four measures of chlorine and one of light carburetted hydrogen are present, carbonic and hydrochloric acid gases will be produced: two volumes of chlorine combine with two volumes of hydrogen contained in the carburetted hydrogen, and the other two volumes of chlorine decompose so much water as will likewise give two volumes of hydrogen, forming hydrochloric acid; while the oxygen of the water unites with the carbon, and converts it into carbonic acid. If there are three instead of four volumes of chlorine, carbonic oxide will be generated instead of carbonic acid, because one-half less water will be decomposed. (Henry.) If a mixture of chlorine and light carburetted hydrogen is electrified or exposed to a red heat, hydrochloric acid is formed, and charcoal deposited.

Its eq. is 8·12; eq. vol. = 100; symb. H_2C.

It was first ascertained by Henry (Nicholson's Journal, vol. xix.);

and his conclusions have been fully confirmed by the subsequent researches of Davy, that the *fire-damp* of coal-mines consists almost solely of light carburetted hydrogen. This gas often issues in large quantity from between beds of coal, and by collecting in mines, owing to deficient ventilation, gradually mingles with atmospheric air, and forms an explosive mixture. The first unprotected light which then approaches sets fire to the whole mass, and an explosion ensues. These accidents, which were formerly so frequent and so fatal, are now comparatively rare, owing to the employment of the safety-lamp. For this invention we are indebted to Davy, who established the principles of its construction by a train of elaborate experiment and close reasoning, which may be regarded as one of the happiest efforts of his genius. (Essay on Flame.)

Davy commenced the inquiry by determining the best proportion of air and light carburetted hydrogen for forming an explosive mixture. When the inflammable gas is mixed with 3 or 4 times its volume of air, it does not explode at all. It detonates feebly when mixed with 5 or 6 times its bulk of air, and powerfully when 1 to 7 or 8 is the proportion. With 14 times its volume, it still forms a mixture which is explosive; but if a larger quantity of air be admitted, a taper burns in it only with an enlarged flame.

The temperature required for causing an explosion was next ascertained. It was found that the strongest explosive mixture may come in contact with iron or other solid bodies heated to redness, or even to whiteness, without detonating, provided they are not in a state of actual combustion; whereas the smallest point of flame, owing to its higher temperature, instantly causes an explosion.

The last important step in the inquiry was the observation that flame cannot pass through a narrow tube. This led to the discovery, that the power of tubes in preventing the transmission of flame is not necessarily connected with any particular length; and that a very short one will have the effect, provided its diameter is proportionally reduced. Thus, a piece of fine wire gauze, which may be regarded as an assemblage of short narrow tubes, is quite impermeable to flame; and, consequently, if a common oil lamp be completely surrounded with a cage of such gauze, it may be introduced into an explosive atmosphere of fire-damp and air, without kindling the mixture. This simple contrivance, which is appropriately termed the *safety-lamp*, not only prevents explosion, but indicates the precise moment of danger. When the lamp is carried into an atmosphere charged with fire-damp, the flame begins to enlarge; and the mixture, if highly explosive, takes fire as soon as it has passed through the gauze, and burns on its inner surface, while the light in the centre of the lamp is extinguished. Whenever this appearance is observed, the miner must instantly withdráw; for though the flame should not be able to communicate with the explosive mixture on the outside of the lamp, as long as the texture of the gauze remains entire, yet the heat emitted during the combustion is so great, that the wire, if exposed to it for a few minutes, would suffer oxidation, and fall to pieces.

The peculiar operation of small tubes in obstructing the passage of flame admits of a very simple explanation. Flame is gaseous matter heated so intensely as to be luminous; and Davy has shewn that the temperature necessary for producing this effect is far higher than the white heat of solid bodies. Now, when flame comes in contact with the sides of very minute apertures, as when wire gauze is laid upon a burning jet of coal gas, it is deprived of so much heat that its temperature instantly falls below the degree at which gaseous matter is luminous; and consequently, though the gas itself passes freely through the interstices, and is still very hot, it is no longer incandescent. Nor does this take place when the wire is cold only; the effect is equally certain at any degree of heat which the flame can communicate to it. For since the gauze has a large extent of surface, and from its metallic nature is a good conductor of heat, it loses heat with great rapidity. Its temperature, therefore, though it may be heated to whiteness, is always so far below that of the flame, as to exert a cooling influence over the burning gas, and reduce its heat below the point at which it is incandescent.

These principles suggest the conditions under which Davy's lamp would cease to be safe. If a lamp with its gauze red-hot be exposed to a *current* of explosive mixture, the flame may possibly pass so rapidly as not to be cooled below the point of ignition, and in that case an accident might occur with a lamp which would be quite safe in a calm atmosphere. It has been lately shewn by Messrs. Upton and Roberts, lamp manufacturers of this city, that flame may in this way be made to pass through the safety-lamp as commonly constructed; and I am satisfied, from having witnessed some of their experiments, that the observation is correct. This then may account for accidents in coal-mines where the safety-lamp is constantly employed. An obvious mode of avoiding such an evil is to diminish the apertures of the gauze; but this remedy is nearly impracticable from the obstacle which very fine gauze causes to the diffusion of light. A better method is to surround the common safety-lamp with a glass cylinder, allowing air to enter solely at the bottom of the lamp through wire gauze of extreme fineness, placed horizontally, and to escape at top by a similar contrivance. Upton and Roberts have constructed a lamp of this kind, through which I have in vain tried to cause the communication of flame, and which appears to me perfectly secure: should an accident break the glass, their lamp would be reduced to a safety-lamp of the common construction. Davy's lamp thus modified gives a much better light than without the glass, just as all lamps burn better with a shade than without one.

The compound commonly called olefiant gas, which contains 2 eq. carbon and 2 eq. hydrogen, will be described in the organic chemistry, among the compounds of acetate, the organic radical of acetic acid.

The other compounds of carbon and hydrogen are also described in the organic chemistry. They belong to this department not only as being products of the organic kingdom, but also on account of their atomic constitution; for whenever they are acted on by chlorine or any other dehydrogenizing agents, one part of the hydrogen, which enters into their composition, is shewn to be in a state of combination different from the rest. Thus, evidence is obtained that these compounds, although composed of nothing but hydrogen and carbon, are not formed by the direct union of these elements, but that a portion of the hydrogen with the carbon forms a compound radical, which acts the part of an element and combines as such with the remainder of the hydrogen.

SECTION III.

COMPOUNDS OF HYDROGEN AND SULPHUR.

Sulphur unites with hydrogen in at least two proportions, and the resulting compounds are thus constituted :—

	Hydrogen.	Sulphur.	Equiv.	Formulæ.
Hydrosulphuric Acid .	1 1 eq. +	16·1	1 eq. = 17·1	HS.
Persulphuret of Hydrogen	1 1 eq. +	32·2	2 eq. = 33·2	HS_2.

Hydrosulphuric Acid.—Hist. and Prep.—Commonly known under the name of sulphuretted hydrogen. It is best prepared by heating sesquisulphuret of antimony in a retort, or other convenient glass vessel, with four or five times its weight of strong hydrochloric acid; when, by an interchange of elements, sesquichloride of antimony and hydrosulphuric acid are generated, the latter of which escapes with effervescence. The elements concerned, before and after the change, are

1 eq. Sesquisulphuret of Antimony and 3 eq. Hydrochloric Acid
Sb_2S_3 $3HCl$,

which yield

3 eq. Hydrosulphuric Acid and 1 eq. Sesquichloride of Antimony
$3HS$ Sb_2Cl_3.

It may also be formed by the action of sulphuric acid diluted with 3 or 4 parts of water on protosulphuret of iron: this sulphuret and water interchange elements, hydrosulphuric acid and protoxide of iron are generated, and the latter unites with sulphuric acid, while the former in the state of gas is rapidly disengaged. Hydrochloric acid may be advantageously substituted for the sulphuric. A sulphuret of iron may be procured for the purpose, either by igniting common iron pyrites, by which means nearly half of its sulphur is expelled, or by exposing to a low red heat a mixture of two parts of iron filings and rather more than one part of sulphur. The materials should be placed in a common earthen or cast-iron crucible, and be protected as much as possible from the air during the process. The sulphuretted hydrogen procured from iron filings and sulphur always contains some uncombined iron, and therefore the gas obtained from it is never quite pure, being mixed with a little free hydrogen. This, however, for many purposes, is immaterial.

Prop.—Colourless gas, which reddens moist litmus paper feebly, and is distinguished from all other gaseous substances by its offensive taste and odour, which is similar to that of putrefying eggs, or the water of sulphurous springs. Under a pressure of 17 atmospheres, at 50°, it is compressed into a limpid liquid, which resumes the gaseous state as soon as the pressure is removed. To animal life it is very injurious. According to Dupuytren and Thenard, the presence of 1-1500th of this gas in air is instantly fatal to a small bird; 1-1000th killed a middle-sized dog; and a horse died in an atmosphere which contained 1-250th of its volume.

It extinguishes all burning bodies; but the gas takes fire when a lighted candle is immersed in it, and burns with a pale blue flame. Water and sulphurous acid are the products of its combustion, and sulphur is deposited. With oxygen gas it forms a mixture which detonates by the application of flame or the electric spark; if 100 measures of it are exploded with 150 of oxygen, the former is completely consumed, the oxygen disappears, water is deposited, and 100 measures of sulphurous acid gas remain. (Thomson.) From the result of this experiment, the composition of hydrosulphuric acid gas may be inferred; for it is clear, from the composition of sulphurous acid, that two-thirds of the oxygen must have combined with sulphur; and, therefore, that the remaining one-third contributed to the formation of water. Consequently, 100 vol. of hydrosulphuric acid contains its own volume of hydrogen gas, and 16·66 of the vapour of sulphur; and since

	Grains.
16·66 cubic inches of the Vapour of Sulphur weigh . . .	34·3610
100 cubic inches of Hydrogen Gas weigh	2·1318
100 cubic inches of Hydrosulp. Acid Gas must weigh . .	36·4928

The sp. gr. of a gas so constituted should be 1·177, which agrees with observation; and its elements are in the ratio of 1 to 16·1, as already mentioned.

The accuracy of this view is confirmed by several circumstances. Thus, according to Gay-Lussac and Thenard, the weight of 100 cubic inches of hydrosulphuric acid gas is 36·33 grains. When sulphur is heated in hydrogen gas, hydrosulphuric acid is generated without any change of volume. On igniting platinum wires in it by means of the voltaic apparatus, sulphur is deposited, and an equal volume of pure hydrogen remains; and a similar effect is produced, though more slowly, by a succession of electric sparks. (Elements of Davy, p. 282.) Gay-Lussac and Thenard found that on heating tin in hydrosulphuric acid gas, sulphuret of tin is formed; and when potassium is heated in it, vivid combustion ensues, with formation of sulphuret of potassium. In both cases, pure hydrogen is left, which occupies precisely the same space as the gas from which it is derived. (Recherches Physico-Chimiques, vol. i.)

The salts of hydrosulphuric acid are called *hydrosulphates*, and sometimes *hydrosulphurets*. This acid, however, rarely unites directly with metallic oxides; but in most cases its hydrogen combines with the oxygen of the oxide and its sulphur with the metal, according to the general formula, $HS + MO = HO + MS$. When sulphuretted hydrogen unites with ammonia, it may be supposed either to do so directly, forming the compound NH_3,HS, which is called hydrosulphuret of ammonia, or to yield its hydrogen, thus producing ammonium, with which the sulphur then unites, as shewn in the equation $NH_3 + HS = NH_4,S$. On this view the compound is termed sulphuret of ammonium. This compound, and many metallic sulphurets are decomposed by sulphuric or hydrochloric acids, and hydrosulphuric acid gas is disengaged with effervescence.

Recently boiled water absorbs its own volume of hydrosulphuric acid, becomes thereby feebly acid, and acquires the peculiar odour and taste of sulphurous springs. The gas is expelled without change by boiling the water.

The elements of hydrosulphuric acid may easily be separated from one another. A solution of the gas cannot be preserved in an open vessel, because its hydrogen unites with the oxygen of the atmosphere, and sulphur is deposited. When mixed with sulphurous acid, both compounds are decomposed, water is generated, and sulphur set free. On pouring into a bottle of the gas a little fuming nitric acid, mutual decomposition ensues, a bluish-white flame frequently appears, sulphur and nitrous acid fumes come into view, and water is generated. Chlorine, iodine, and bromine decompose it, with separation of sulphur, and formation of hydrochloric, hydriodic, and hydrobromic acids. An atmosphere charged with hydrosulphuric acid gas may be purified by means of chlorine in the space of a few minutes.

Hydrosulphuric acid gas is readily distinguished from other gases by its odour, by tarnishing silver with which it forms a sulphuret, and by the character of the precipitate which it produces with solutions of arsenious acid, tartar emetic, and salts of lead. The most delicate test of its presence, when diffused in the air, is moist carbonate of oxide of lead spread on white paper.

Its eq. is 17·1; eq. vol. $=100$; symb. HS.

Persulphuret of Hydrogen.—Hist. and Prep.—Discovered by Scheele, but first specially described by Berthollet. (An. de Chimie, xxv.) When protosulphuret of potassium (or of any metal of the alkalies and alkaline earths) is mixed in solution with sulphuric acid, the oxygen of water unites with potassium and its hydrogen with sulphur, just as when protosulphuret of iron is employed, hydrosulphuric acid and sulphate of potassa being generated: the elements $K+S$ and $H+O$ mutually interchange, and yield $K+O$ and $H+S$. If the potassium be combined with two or more equivalents of sulphur as in the so called *liver of sulphur*, made by fusing carbonate of potassa with half of its weight of sulphur, then one of two events will happen: the hydrogen of the decomposed water will either unite with 1 eq. of sulphur and form hydrosulphuric acid, the superfluous sulphur subsiding in the form of a grey hydrate, or with 2 eqs. of sulphur, and give rise to persulphuret of hydrogen. Now, the former of these changes always occurs when the acid is added to the persulphuret of potassium; and the latter takes place when a concentrated solution of that sulphuret is added by little and little to the acid, provided the acid is in considerable excess, and the mixture well stirred after each addition. The same phenomena ensue when hydrochloric instead of sulphuric acid is employed; but then there are two sources from which hydrogen may be supplied. It may be derived, as above, from decomposed water, hydrochlorate of potassa being generated; or hydrochloric acid itself may be decomposed, its hydrogen uniting with sulphur and its chlorine with potassium. On all such occasions I adopt the latter view, and will give reasons for doing so in the section introductory to the study of the metals.

Such are the principles to be attended to in preparing persulphuret of hydrogen. In practice it is conveniently made by boiling equal parts of recently slaked lime and flowers of sulphur with 5 or 6 parts of water for half an hour, when a deep orange-yellow solution is formed, which contains persulphuret of calcium. Let this liquid be filtered, and gradually added cold to an excess of hydrochloric acid diluted with about twice its weight of water, briskly stirring. A copious deposit of sulphur falls (the sulphur præcipitatum of the London Pharmacopœia), and persulphuret of hydrogen gradually subsides in the form of a yellowish semi-fluid matter like oil. The change which ensues in the formation of the yellow solution may be theoretically represented thus:—

2 eq. lime and 6 eq. Sulphur yield 1 eq. Hyposulph. Acid and 2 eq. Bisulphuret Calcium
$2CaO + S_6$ yield $S_2O_2 + 2CaS_2$.

The hyposulphurous acid exists in solution united with lime, and is decomposed when hydrochloric acid is added, resolving itself into sulphurous acid and sulphur; a change not essentially connected with the production of persulphuret of hydrogen, but resulting from the mode of preparing the persulphuret of calcium. It is probable that the calcium is combined with more than 2 eqs. of sulphur, and that the deposited sulphur is derived from that source, as well as from decomposed hyposulphurous acid.

Prop.—From the facility with which this substance resolves itself into sulphur and hydrosulphuric acid, its history is imperfect: we are indebted to an essay by Thenard for the principal facts which are known. (An. de Ch. et Ph. xlviii. 79.) At common temperatures it is a viscid liquid, of a yellow colour, with a density of about 1·769, and a consistence varying between that of a volatile and fixed oil. It has the peculiar odour and taste of hydrosulphuric acid, though in a less degree. Its elements are so feebly united, that in the cold it gradually resolves itself into sulphur and hydrosulphuric acid, and suffers the same change instantly by a heat considerably short of 212° F. Decomposition is also produced by the contact of most substances, especially of metals, metallic oxides, even the alkalies, and metallic sulphurets. Thus, effervescence from the escape of hydrosulphuric acid gas is produced by peroxide of manganese, silica, the alkaline earths in powder, and solutions of potassa or soda; and the oxides of gold and silver are reduced by it with such energy, that they are rendered incandescent. It is remarkable that the substance which causes the decomposition often undergoes no chemical change whatever. In these respects persulphuret of hydrogen bears a close analogy to peroxide of hydrogen; and Thenard has traced other points of resemblance. They are both, for instance, rendered more stable by the presence of acids; they both whiten the tongue and skin when applied to them, and they are both possessed of bleaching properties.

The composition of persulphuret of hydrogen has been variously stated. According to Dalton it is a bisulphuret, consisting of two equivalents of sulphur and one of hydrogen; and this view of its composition is corroborated by Sir John Herschel's analysis of persulphuret of calcium. (Edin. Phil. Journal, i. 13.) But Thenard found its constituents to vary; whence it is probable that hydrogen is capable of uniting with sulphur in several proportions.

Persulphuret of hydrogen is sometimes regarded as an acid; and on this supposition it may be termed *hydropersulphuric acid*, and its salts *hydropersulphates.* This view is founded on the hypothesis, that the solutions formed by boiling lime or an alkali with sulphur contain hyposulphite and hydropersulphate of lime, the hydrogen in the one acid and oxygen in the other being attributed to decomposed water, and not hyposulphite of lime and persulphuret of calcium, as I have supposed. The latter view is more consistent with the fact that persulphuret of hydrogen in its free state has no acidity, and exhibits no tendency to unite with alkalies.

Its eq. is $=33{\cdot}2$; symb. HS_2; but according to some chemists its formula is HS_5, and its eq. 81·5. Its true composition must be considered doubtful.

SECTION IV.

HYDROGEN AND SELENIUM.—HYDROSELENIC ACID.

Selenium, like sulphur, forms a gaseous compound with hydrogen, which has distinct acid properties, and is termed *seleniuretted hydrogen* or *hydroselenic acid.* It is disengaged by the action of dilute sulphuric or hydrochloric acid on a protoseleniuret of any of the more oxidable metals, such as potassium, calcium, manganese, or iron, the explanation being the same as in the formation of hydrosulphuric acid from protosulphuret of iron.

Hydroselenic acid gas is colourless. Its odour is at first similar to that of hydrosulphuric acid; but it afterwards irritates the lining membrane of the nose powerfully, excites catarrhal symptoms, and destroys for some hours the sense of smelling. It is absorbed freely by water, forming a colourless solution, which reddens litmus paper, and gives a brown stain to the skin. The acid is soon decomposed by exposure to the atmosphere; for the oxygen of the air unites with the hydrogen of the hydroselenic acid, and selenium, in the form of a red powder, subsides. It is decomposed by nitric acid and chlorine in the same manner as hydrosulphuric acid ; and, like that gas, it decomposes many metallic salts, the hydrogen of the acid combining with the oxygen of the oxide, while an insoluble seleniuret of the metal is generated.

According to the analysis of Berzelius, hydroselenic acid consists of 39·6 parts or 1 eq. of selenium, and 1 part or 1 eq. of hydrogen : so that its eq. is 40·6 ; its symb. HSe.

SECTION V.

COMPOUNDS OF HYDROGEN AND PHOSPHORUS.

The existence of two compounds of phosphorus and hydrogen, the phosphuretted and perphosphuretted hydrogen, have, until lately, been generally admitted by chemists. Their composition and properties have been closely studied by Dumas, Buff, Rose, and Graham. (An. de Ch. et Ph. xxxi. 113 ; xli. 220 ; and xli. 5. Phil. Mag. v. 401.) The investigations of these chemists concurred in proving that phosphuretted hydrogen consists of 31·4 parts or 1 eq. of phosphorus, and 3 parts or 3 eqs. of hydrogen ; while the discordancy in their analyses of perphosphuretted hydrogen caused great uncertainty respecting its constitution. Thus, although Dumas and Rose agree that 100 measures of perphosphuretted hydrogen contain 150 measures of hydrogen, the former states that 1 part of hydrogen is united with 15·9 of phosphorus, the latter with 10·52, while Thomson estimates the quantity at 12. The result of Rose would indicate that the two compounds of phosphorus and hydrogen are isomeric, being identical in composition, and differing in character only by the one being spontaneously inflammable, and the other not so. The accuracy of the analytical results of Rose have been recently established by the discoveries of Leverrier (An. de Ch. et Ph. lx. 174), who has proved that perphosphuretted hydrogen is a mixture of phosphuretted hydrogen with about $\frac{1}{30}$ of its volume of a spontaneously inflammable compound, which he considers to be composed of 31·4 parts or 1 eq. of phosphorus, and 2 parts or 2 eqs. of hydrogen. In the same paper he establishes the existence of a compound formed of 31·4 parts or 1 eq. of phosphorus, and 1 part or 1 eq. of hydrogen. The compounds of phosphorus and hydrogen are, therefore,

		Phos.		Hyd.		Equiv.	Formulæ.
Solid Phosphuretted Hydrogen	.	31·4	1 eq. +	1	1 eq. =	32·4	PH.
Inflammable . do. .	.	31·4	1 eq. +	2	2 eq. =	33·4	PH_2.
Gaseous . do. .	.	31·4	1 eq. +	3	3 eq. =	34·4	PH_3.

Solid Phosphuretted Hydrogen.—When phosphuretted hydrogen gas, recently prepared by the action of quicklime and phosphorus, is exposed in the moist state to a strong diffused light, or to the direct rays of the sun, the solid phosphuretted hydrogen is deposited on the sides of the glass vessel. It is also left as an insoluble powder when phosphuret of potassium is dissolved in water. As obtained by the former process it is a canary yellow flocculent matter, is insoluble in water and alcohol; but with the former a slow oxidation takes place, and hydrogen is evolved. It is not altered by a temperature of 234°, but heated beyond that point it is decomposed. When brought into contact with chlorine and nitric acid it suffers instantaneous decomposition. According to the analysis of Leverrier, it is composed of 1 part or 1 eq. of hydrogen, and 31·4 parts or 1 eq. of phosphorus. Hence its eq. is 32·4; symb. PH.

PHOSPHURETTED HYDROGEN.

Hist. and Prep.—Discovered by Davy in 1812. It may be prepared by several methods. Davy prepared it by heating hydrated phosphorous acid in a retort; and it is evolved from hydrous hypophosphorous acid by similar treatment, and by the action of strong hydrochloric acid on phosphuret of calcium according to Dumas. It may also be obtained, but in an impure state, by boiling phosphorus with a solution of potassa or milk of lime. Its production is in these cases dependent on the decomposition of water, the oxygen and hydrogen of which unite with different portions of phosphorus, and phosphoric acid, hypophosphorous acid, and phosphuretted hydrogen are generated.

Prop.—A transparent colourless gas of an exceedingly offensive odour and bitter taste. It has no action on test paper. It is absorbed in small quantity by water, but freely by solutions of chloride of calcium or sulphate of the oxide of copper, by which means its purity may be ascertained. Like sulphuretted hydrogen, it frequently decomposes metallic salts, giving rise to the formation of water and a phosphuret of the metal. But if the metal have a feeble affinity for oxygen, it is thrown down in the metallic state, and water and phosphoric acid are generated. This is the case, according to Rose, with solutions of gold and silver.

It is a non-supporter of combustion, and is very destructive to animal life. When pure, it may be mixed with air or oxygen gas at common temperatures without danger; but the mixture detonates with the electric spark, or at a temperature of 300°. Even diminished pressure causes an explosion; an effect which, in operating with a mercurial trough, is produced simply by raising the tube, so that the level of the mercury within may be a few inches higher than at the outside. Such is the property of the pure gas, as obtained from the hydrated phosphorous or hypophosphorous acids; but if it be procured from the action of phosphorus on potassa or hydrate of lime, it is remarkable for being spontaneously inflammable when mixed with air or oxygen gas. If the beak of the retort from which it issues is plunged under water, so that successive bubbles of the gas may arise through the liquid, a very beautiful appearance takes place. Each bubble, on reaching the surface of the water, bursts into flame, and forms a ring of dense white smoke, which enlarges as it ascends, and retains its shape, if the air is tranquil, until it disappears. The wreath is formed by the products of the combustion—metaphosphoric acid and water. If received in a vessel of oxygen gas, the entrance of each bubble is instantly followed by a strong concussion, and a flash of white light of extreme intensity. It is remarkable that whatever may be the excess of oxygen, traces of phosphorus always escape combustion; but that if the gas be previously mixed with three times its volume of carbonic acid, and be then mixed with oxygen, the combustion is perfect. Dalton observed that it may be mixed with pure oxygen in a tube three-tenths of an inch in diameter without taking fire; but that the mixture detonates when an electric spark is transmitted through it.

In consequence of the combustibility of phosphuretted hydrogen it would be hazardous to mix it in any quantity with air or oxygen gas in close vessels. For the same reason care is necessary in the formation of this gas, lest, in mixing with the air of the apparatus, an explosion ensue, and the vessel burst. The risk of such an accident is avoided, when phosphuret of calcium is used, by filling the flask or retort entirely with dilute acid; and in either of the other processes, by causing the phosphuretted hydrogen to be formed slowly at first, in order that the oxygen gas within the apparatus may be gradually consumed. A very simple method of averting all danger has been mentioned by Graham. It consists in moistening the interior of the retort with one or two drops of ether, the vapour of which, when mixed with atmospheric air even in small proportion, effectually prevents the combustion of phosphuretted hydrogen. The same effect may be produced by the addition of several other bodies. He also finds that a gas, which is not spontaneously inflammable, acquires this property on being mixed with from $\frac{1}{1000}$ to $\frac{1}{10000}$ of its volume of nitrous acid. According to Leverrier, it is very probable that there exists a compound of phosphorus and hydrogen composed of 1 eq. of phosphorus and 2 of hydrogen, and that this compound being spontaneously inflammable communicates that property to phosphuretted hydrogen gas. This opinion is grounded on the fact that when spontaneously inflammable phosphuretted hydrogen is kept for any length of time in a dark place it suffers no change, but if brought into a strong light solid phosphuretted hydrogen is deposited, and the residual gas is no longer spontaneously inflammable. Thus, it appears that by the action of light PH_2 is decomposed, and PH and PH_3 are formed. The result of his analysis supports this view.

Dumas ascertained the composition of phosphuretted hydrogen by introducing into a tube containing the gas a fragment of bichloride of mercury, and applying heat so as to convert it into vapour. Mutual decomposition instantly took place: phosphuret of mercury and hydrochloric acid were generated; and 100 measures of gas, thus decomposed, yielded 300 measures of hydrochloric acid gas, corresponding to 150 of hydrogen. The quantity of hydrogen contained in any given volume of phosphuretted hydrogen is thus found; and the weight of the former deducted from that of the latter gives the quantity of combined phosphorus. This inference is conformable to the quantity of oxygen required for the combustion of phosphuretted hydrogen. Thomson affirms that when this gas is detonated with 1·5 of its volume of oxygen gas, the only products are water and phosphorous acid; but that when the oxygen is in considerable excess, two volumes disappear for one of the compound, and water and phosphoric acid are generated. Now the hydrogen contained in one volume of phosphuretted hydrogen is equal to 1·5, and it unites with 0·75 of oxygen. Hence, if 0·75, or $\frac{3}{4}$, be deducted from 1·5 and from 2, the remainders, $\frac{3}{4}$ and $\frac{5}{4}$, represent the relative quantity of oxygen which is required to convert the same weight of phosphorus into phosphorous and phosphoric acid. These numbers are obviously in the ratio of 3 to 5, as already stated on the authority of Berzelius. The elements of the calculation have been confirmed both by Dumas and Buff.

Agreeably to these views, and to the combining volume of phosphorus (page 163), 100 measures of phosphuretted hydrogen gas contain 150 of hydrogen gas and 25 of the vapour of phosphorus; and hence, as

			Grains.
150	cubic inches of	Hydrogen Gas weigh	3·1977
25	do.	Phosphorus Vapour weigh	33·5425
100	do.	Phosphuretted Hydrogen Gas should weigh . .	36·7402

The calculated density of a gas so constituted should be 1·1853, which is nearly a mean of the observations of Dumas and Rose.

As the equivalent now assumed for phosphorus in this work is 31·4, instead of the number 15·7 formerly admitted, the combining volume of phosphorus vapour, in the table, p. 163, has been altered to 50 instead of 25 as formerly, and hence phosphuretted hydrogen consists of 300 volumes of hydrogen united with 50 of phosphorus vapour, condensed into 300 volumes, which is the same proportion as 150 to 25 above given. Its formula, taking the new equivalent of phosphorus, is PH_3, analogous to that of ammonia, NH_3, although the composition by volume, owing to the great density of phosphorus vapour, and its consequently small combining volumes, is different.

Phosphuretted hydrogen has neither an acid nor alkaline reaction, but in its chemical relations it inclines to alkalinity. Thus, it unites with hydrobromic and hydriodic acids, forming definite compounds which crystallize in cubes; and Rose finds that it unites with metallic chlorides, forming compounds analogous to those which ammonia forms with metallic chlorides.

Its eq. is 34·4; eq. vol. = 100; symb. $P + 3H$, or PH_3.

SECTION VI.

COMPOUNDS OF NITROGEN AND CARBON.

BICARBURET OF NITROGEN, OR CYANOGEN GAS.

Hist. and Prep.—Discovered in 1815 by Gay-Lussac. (An. de Ch. xcv.) It is prepared by heating carefully dried bicyanuret of mercury in a small glass retort by means of a spirit-lamp. This cyanuret, which was formerly considered a compound of oxide of mercury and prussic acid, and was then called *prussiate of mercury*, is composed of metallic mercury and cyanogen. On exposure to a low red heat it is resolved into its elements; the cyanogen passes over in the form of gas, and the metallic mercury is sublimed. The retort, at the close of the process, contains a small residue of a dark brown matter like charcoal, but which Johnston has shewn to consist of the same ingredients as the gas itself.

Prop.—A colourless gas, possessing a strong pungent and very peculiar odour. At the temperature of 45°, and under a pressure of 3·6 atmospheres, it is a limpid liquid, which Kemp finds to be a non-conductor of electricity, and which resumes the gaseous form when the pressure is removed. It extinguishes burning bodies; but it is inflammable, and burns with a beautiful and characteristic purple flame.

It can support a strong heat without decomposition. Water at the temperature of 60° absorbs 4·5 times, and alcohol 23 times its volume of the gas. The aqueous solution reddens litmus paper; but this effect is not to be ascribed to the gas itself, but to the presence of acids which are generated by the mutual decomposition of cyanogen and water. The products of this spontaneous decomposition are very numerous. They will be described in the second part of this work.

The composition of cyanogen may be determined by mixing that gas with a due proportion of oxygen, and inflaming the mixture by electricity. Gay-Lussac ascertained in this way that 100 measures of cyanogen require 200 of oxygen for complete combustion, that no water is formed, and that the products are 200 measures of carbonic acid gas and 100 of nitrogen. Hence it follows that cyanogen contains its own bulk of nitrogen, and twice its volume of the vapour of carbon. Consequently, since

	Grains.
100 cubic inches of Nitrogen Gas weigh	30·166
200 do. the Vapour of Carbon weigh	26·306
100 cubic inches of Cyanogen Gas must weigh	56·472

The ratio of its elements by weight is,

Nitrogen .	30·166 . .	0·9727 . .	14·15	1 eq.
Carbon .	26·306 . .	0·8430 (2 + 0·4215)	12·24	2 eq.

The sp. gr. of a gas so constituted is 0·9727 + 0·843 = 1·8157, which is near 1·8064, the number found experimentally by Gay-Lussac.

Cyanogen is a *bicarburet of nitrogen*, the formula of which is N + 2C, or NC_2; but its most convenient name is *cyanogen*, proposed by its discoverer,* which may be expressed shortly by Cy. Its eq. is 26·39.

Paracyanogen.—An examination of the brown matter, left in the retort after the preparation of cyanogen gas, has been made by Johnston, who by burning it with chlorate of potassa found it to contain carbon and nitrogen united in the same ratio as in cyanogen gas. It is, in fact, a solid bicarburet of nitrogen, isomeric with cyanogen, but differing from it essentially in its physical and chemical relations. On heating this solid bicarburet in the open air, several definite compounds of carbon and nitrogen may be successively obtained. After considerable heating, the ratio of carbon to nitrogen is as 3 to 2; again heated, the proportion becomes as 7 to 6; and finally, after a still longer heat, the ratio of the equivalents is as 1 to 1. Thus the carbon is gradually burned away, leaving the nitrogen fixed, until a protocarburet of nitrogen is formed. On continuing the heat after this period, both elements fly off together, and the whole is dissipated. The solid bicarburet of cyanogen is also generated, when a saturated solution of cyanogen in alcohol is kept in contact with mercury; and Johnston suggests that the carbonaceous residue after the charring of animal substances by heat is probably in many cases a carburet of nitrogen, and not pure charcoal as is commonly thought. (Brewster's Journ., N.S., i. 75.) Paracyanogen is soluble in sulphuric and nitric acids, and forms a compound with oxygen in which 1 eq. of oxygen is combined with 4 eqs. of nitrogen and 8 eqs. of carbon. Hence the eq. of paracyanogen is probably 105·56, and its symb. N_4C_8.

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* From κυανος *blue*, and γενναω *I generate;* because it is an essential ingredient of Prussian blue.

Mellon—Is obtained when sulphuret of cyanogen, melame, melamine, ammeline, or ammelide is exposed to a red heat. It is a lemon-yellow powder, is insoluble in water and alcohol, but is dissolved and decomposed by acids and alkalies. Exposed to a strong red heat, it is decomposed and forms 1 vol. of nitrogen and 3 vols. of cyanogen gas. It is one of the compound radicals. Its eq. is 93·32; symb. N_4C_6. (Lieb. An. ix. 5.)

Cyanogen, though a compound body, has a remarkable tendency to combine with elementary substances. Thus it is capable of uniting with the simple non-metallic bodies, and evinces a strong attraction for metals. When potassium, for instance, is heated in cyanogen gas, such energetic action ensues, that the metal becomes incandescent, and cyanuret of potassium is generated. The affinity of cyanogen for metallic oxides, on the contrary, is comparatively feeble. It enters into direct combination with a few alkaline bases only, and these compounds are by no means permanent. From these remarks it is apparent that cyanogen has no claim to be regarded as an acid, as it has none of the properties of a compound. It is, in fact, a compound radical of organic chemistry, and therefore its various combinations will be described in that part of the work.

SECTION VII.

COMPOUND OF PHOSPHORUS AND NITROGEN.

Phosphuret of Nitrogen.—First described by Rose. (Pogg. An. xxviii. 529.) On saturating either of the chlorides of phosphorus with dry ammoniacal gas, a white solid mass is obtained, which on exposure to a strong red heat gives rise to the formation of phosphuret of nitrogen, hydrochloric acid gas being at the same time evolved. It is also formed when the vapour of either of the chlorides of phosphorus is brought into contact with sal-ammoniac heated nearly to its point of sublimation.

It is a light snow-white powder; is insoluble in water, and in dilute acid, or alkaline solutions. It is not changed by a red heat in close vessels, or in an atmosphere of chlorine, or the vapour of sulphur; but in hydrogen it is decomposed with the formation of ammoniacal gas. It is composed of 31·4 parts or eq. of phosphorus, and 14·15 parts or 1 eq. of nitrogen.

Its eq. is 45·55; symb. N + P, or NP.

SECTION VIII.

COMPOUNDS OF SULPHUR, CARBON, ETC.

The compounds described in this section are thus constituted:—

Bisulph. of Carbon	Carb. 6·12 + Sulp. 32·2 = 38·32	C + 2S CS_2.
Sulph. of Phosphorus	Composition uncertain.	
Bisulph. of Selenium	Selen. 39·6 + Sulp. 32·2 = 71·8	Se + 2S SeS_2.
Seleni. of Phosphorus	Composition uncertain.	

Bisulphuret of Carbon.—*Hist.*—This substance was discovered accidentally in the year 1796 by Professor Lampadius, who regarded it as a compound of sulphur and hydrogen, and termed it *alcohol of sulphur.* Clément and Desormes first declared it to be a sulphuret of carbon, and their statement was fully confirmed by the joint researches of Berzelius and the late Dr. Marcet. (Phil. Trans., 1813.)

Prep.—Bisulphuret of carbon may be obtained by heating in close vessels native bisulphuret of iron (iron pyrites) with one-fifth of its weight of well-dried charcoal; or by transmitting the vapour of sulphur over fragments of charcoal heated to redness in a tube of porcelain. The compound, as it is formed, should be conducted by means of a glass tube into cold water, under which it is collected. To free it from moisture and adhering sulphur, it should be distilled at a low temperature in contact with chloride of calcium.

Prop.—It is a transparent colourless liquid, which is remarkable for its high refractive power. Its sp. gr. is 1·272; that of its vapour, 2·668. It has an acid, pungent, and somewhat aromatic taste, and a very fœtid odour. It is exceedingly volatile; its vapour at 63·5° supports a column of mercury 7·36 inches long; and at 110° it enters into brisk ebullition. From its great volatility it produces intense cold by its evaporation. It is very inflammable, and kindles in the open air at a temperature scarcely exceeding that at which mercury boils. It burns with a pale blue flame. Admitted into a vessel of oxygen gas, so much vapour rises as to form an explosive mixture; and when mixed in like manner with binoxide of nitrogen, it forms a combustible mixture, which is kindled on the approach of a lighted taper, and burns rapidly, with a large greenish-white flame of dazzling brilliancy. It dissolves readily in alcohol and ether, and is precipitated from the solution by water. It dissolves sulphur, phosphorus, and iodine, and the solution of the latter has a beautiful pink colour. Chlorine decomposes it, with formation of chloride of sulphur. The pure acids have little action upon it. By nitro-hydrochloric acid it is changed into a white crystalline substance like camphor, which Berzelius regards as a compound of the hydrochloric, carbonic, and sulphurous acids.

Bisulphuret of carbon is a sulphur-acid, that is, unites with *sulphur-bases* to constitute compounds analogous to ordinary salts, and hence called *sulphur-salts.* Thus bisulphuret of carbon unites with sulphuret of potassium, forming a sulphur-salt, in which the former acts as an acid and the latter as a base. The same compound is formed by the action of bisulphuret of carbon on a solution of pure potassa: but in this case sulphuret of potassium is first generated by an interchange of elements with a portion of bisulphuret of carbon, carbonic acid being produced at the same time. Thus—

2 eq. potassa and 1 eq. Bisulph. Carbon yield 2 eq. Sulphuret Potassium and 1 eq. Carb. Acid
$2KO + CS_2$ yield $2KS + CO_2$.

If the bisulphuret of carbon is in sufficient quantity, carbonic acid gas is disengaged, and a neutral compound results. Such is inferred to be the nature of the change, agreeably to the researches of Berzelius on the sulphur-salts.

Its eq. is 38·32; eq. vol. = 100; symb. CS_2.

Sulphuret of Phosphorus.—When sulphur and phosphorus are heated together under water, they readily unite, sometimes with incandescence, and give rise to several compounds, all of which are highly inflammable, and possess a tendency to explode most violently, when heated, from some cause not yet understood. Berzelius has lately published an elaborate paper on this subject, and has described the following compounds:—

1. P_2S. This body occurs in two distinct modifications; one a colourless liquid, the other a red powder. 2. PS. This compound also exhibits two modifications, appearing as a pale yellow fluid, and as an orange powder. 3. PS_{12}. This forms yellow crystals. 4. P_3S_2, apparently a compound of nos. 1 and 2, $P_2S + PS$. It is a scarlet powder, which, when distilled, assumes the shape of a liquid. 5. PS_3.

A yellow solid, very fusible. 6. PS_5. This compound forms yellow crystals.

The very remarkable fact that so many of these singular compounds exist in two modifications, may be accounted for, either by supposing a difference in the absolute number of atoms in an eq. of the two modifications having the same composition; thus no. 1 may be in one state P_2S, and in the other P_4S_2; or by supposing that in some of these compounds, the sulphur, or the phosphorus, or both, may be in some of the alotropic conditions formerly described. The latter view appears the more probable: and a diligent study of these compounds would probably throw much light on some very interesting questions.

Bisulphuret of Selenium.—Sulphur and selenium mix together in all proportions by fusion, and therefore by such means it is difficult to procure a definite compound; but the bisulphuret of an orange colour was formed by Berzelius by precipitating a solution of selenious acid with hydrosulphuric acid. The sulphuret found by Stromeyer among the volcanic products of the Lipari Isles is probably similar in composition. Bisulphuret of selenium fuses at a heat a little above 212°, and at a higher temperature may be sublimed without change. In the open air it takes fire when heated, and sulphurous, selenious, and selenic acids are the products of its combustion. The alkalies and soluble metallic sulphurets dissolve it. Nitric acid acts upon it with difficulty; but the nitro-hydrochloric acid converts it into sulphuric and selenious acids. (An. of Phil. xiv.)

Seleniuret of Phosphorus.—This compound may be prepared in the same manner as the sulphuret of phosphorus; but, as selenium is capable of uniting with phosphorus in several proportions, the compound formed by fusing them together can hardly be supposed to be of a definite nature. The seleniuret is very fusible, sublimes without change in close vessels, and is inflammable. It decomposes water gradually when digested in it, giving rise to seleniuretted hydrogen, and one of the acids of phosphorus.

Sulphuret of Nitrogen.—This compound is formed, according to Soubeiran, by the action of water on a compound of chloride of sulphur and ammonia, $SCl + 2NH_3$. The sulphuret of nitrogen is a yellow or green solid, the colour of which varies according to the mode of preparation. It is converted, by digestion with water, entirely into hyposulphurous acid and ammonia; hence its composition is NS_3 and $2NS_3 + 6HO = 2NH_3 + 3S_2O_2$.

When aqua ammoniæ acts on chloride of sulphur a red solid compound is formed, which is composed of chloride of sulphur, sulphuret of nitrogen, and ammonia. This body undergoes spontaneous decomposition, and is converted into a yellow pulverulent mass. (Soubeiran.) When this mass, which consists chiefly of sulphur, is boiled with alcohol, or exhausted by percolation with cold alcohol, the alcohol dissolves a substance in small quantity, which may be had in white needles or cubical crystals, and which contains 92 — 93 p. c. sulphur and 5 — 6 p. c. nitrogen. Gregory, who discovered this compound, thought that it might be a sulphuret of nitrogen. But in its analysis he always obtained a little hydrogen, and the nature of this substance was left unsettled. Soubeiran is of opinion that it contains sulphur, nitrogen, and ammonia. The quantity of sulphur, however, is so large, that its constitution must be unusual, and it merits a careful examination. Gregory shewed that its solution in alcohol, when mixed with an alcoholic solution of caustic potash, acquires a deep amethyst colour, which soon disappears, while ammonia is set free, pure hyposulphite of potash is deposited, and traces of a volatile compound, probably formed at the expense of the alcohol, are observed.

METALS.

GENERAL PROPERTIES OF METALS.

Metals are distinguished from other substances by the following properties. They are all conductors of electricity and heat. When the compounds which they form with oxygen, chlorine, iodine, sulphur, and similar substances are submitted to the action of galvanism, the metals always appear at the negative side of the battery, and are hence said to be positive electrics. They are quite opaque, refusing a passage to light, though reduced to very thin leaves. They are in general good reflectors of light, and possess a peculiar lustre, which is termed the metallic lustre.—Every substance in which these characters reside may be regarded as a metal.

The number of metals, the existence of which is admitted by chemists, amounts, including several lately discovered, the existence of some of which, as distinct metals, although highly probable, is not yet fully proved, to forty-eight. The following table contains the names of those that have been procured in a state of purity, together with the date at which they were discovered, and the names of the chemists by whom the discovery was made.

Table of the Discovery of Metals.

Names of Metals.	Authors of the Discovery,	Dates of the Discovery.
Gold	Known to the Ancients.	
Silver		
Iron		
Copper		
Mercury		
Lead		
Tin		
Antimony	Described by Basil Valentine	1490
Bismuth	Described by Agricola	1530
Zinc	First mentioned by Paracelsus	16th century
Arsenic	Brandt	1733
Cobalt		
Platinum	Wood, assay-master, Jamaica	1741
Nickel	Cronstedt	1751
Manganese	Gahn and Scheele	1774
Tungsten	D'Elhuyart	1781
Tellurium	Müller	1782
Molybdenum	Hielm	1782
Uranium	Klaproth	1789
Titanium	Gregor	1791
Chromium	Vauquelin	1797

Table of the Discovery of Metals (continued).

Names of Metals.	Authors of the Discovery.	Dates of the Discovery.
Columbium	Hatchett	1802
Palladium	Wollaston	1803
Rhodium		
Iridium	Descotils and Smithson Tennant	1803
Osmium	Smithson Tennant	1803
Cerium	Hisinger and Berzelius	1804
Potassium	Davy	1807
Sodium		
Barium		
Strontium		
Calcium		
Cadmium	Stromeyer	1818
Lithium	Arfwedson	1818
Zirconium	Berzelius	1824
Aluminium	Wöhler	1828
Glucinium		
Yttrium		
Thorium	Berzelius	1829
Magnesium	Bussy	1829
Vanadium	Sefström	1830
Lantanium	Mosander	1839
Didymium	Mosander	since 1840
Erbium		
Terbium		
Ruthenium	Klaus	1844
Pelopium	H. Rose	1845
Niobium		

Most of the metals are remarkable for their great sp. gravity; some of them, such as gold, platinum, or iridium, which are the densest bodies known in nature, being more than 19 times heavier than an equal bulk of water. Great density was once supposed to be an essential characteristic of metals; but the discovery of potassium and sodium, which are so light as to float on the surface of water, has shewn that this supposition is erroneous. Some metals experience an increase of density to a certain extent when hammered, their particles being permanently approximated by the operation. On this account, the density of some of the metals contained in the following table is represented as varying between two extremes.

Table of the Specific Gravity of Metals at 60° Fahr. compared to Water as Unity.

Platinum	20·98	Brisson.
Gold	19·257	Do.
Tungsten	17·6	D'Elhuyart.
Mercury	13·568	Brisson.
Palladium	11·3 to 11·8	Wollaston.
Lead	11·352	Brisson.
Silver	10·474	Do.
Bismuth	9·822	Do.
Uranium	9·000	Bucholz.
Copper	8·895	Hatchett.
Cadmium	8·604	Stromeyer.

Table of the Specific Gravity of Metals, &c.—(continued.)

Cobalt	8·538	Haüy.
Arsenic	5·8843	Turner.
Nickel	8·279	Richter.
Iron	7·788	Brisson.
Molybdenum	7.400	Hielm.
Tin	7.291	Brisson.
Zinc	6·861 to 7·1	Do.
Manganese	6·850	Bergmann.
Antimony	6·702	Brisson.
Tellurium	6·115	Klaproth.
Titanium	5·3	Wollaston.
Sodium	0·972	Gay-Lussac and
Potassium	0·865	Thenard.

Some metals possess the property of *malleability*, that is, admit of being beaten into thin plates or leaves by hammering. The malleable metals are gold, silver, copper, tin, platinum, palladium, cadmium, lead, zinc, iron, nickel, potassium, sodium, and frozen mercury. The other metals are either malleable in a very small degree only, or, like antimony, arsenic, and bismuth, are actually brittle. Gold surpasses all metals in malleability: one grain of it may be extended so as to cover about 52 square inches of surface, and to have a thickness not exceeding $\frac{1}{282020}$th of an inch.

Nearly all malleable metals may be drawn out into wires, a property which is expressed by the term *ductility*. The only metals which are remarkable in this respect are gold, silver, platinum, iron, and copper. Wollaston devised a method by which gold wire may be obtained so fine that its diameter shall be only $\frac{1}{5000}$th of an inch, and that 550 feet of it are required to weigh one grain. He obtained a platinum wire so small, that its diameter did not exceed $\frac{1}{30000}$th of an inch. (Phil. Trans., 1813.) It is singular that the ductility and malleability of the same metal are not always in proportion to each other. Iron, for example, cannot be made into fine leaves, but it may be drawn into very small wires.

The tenacity of metals is measured by ascertaining the greatest weight which a wire of a certain thickness can support without breaking. According to the experiments of Guyton-Morveau, whose results are comprized in the following table, iron, in point of tenacity, surpasses all other metals.

The diameter of each wire was 0·787th of a line.

	Pounds.
Iron wire supports	549·25
Copper	302·278
Platinum	274·32
Silver	187·137
Gold	150·753
Zinc	109·54
Tin	34·63
Lead	27·621

According to some recent observations of Baudrimont, the process of annealing destroys the tenacity of metals to a considerable extent. Thus he found that a wire of soft iron which supported a weight of 26 lbs., on being annealed could only bear 12 lbs.; and a copper wire which could support 22 lbs. was broken, when annealed, by 9 lbs. Numerous experiments with different specimens of brass wire confirm the generality of the result. (An. de Ch. et Ph. lx. 78.)

Metals differ also in hardness; but I am not aware that their exact relation to each other, under this point of view, has been determined by experiment. In the list of hard metals may be placed titanium, manganese, iron, nickel, copper, zinc, and palladium. Gold, silver, and platinum are softer than these; lead is softer still, and potassium and sodium yield to the pressure of the fingers. The properties of elasticity and sonorousness are allied to that of hardness. Iron and copper are in these respects the most conspicuous.

Many of the metals have a distinctly crystalline texture. Iron, for example, is fibrous; and zinc, bismuth, and antimony are lamellated. Metals are sometimes obtained also in crystals; and most of them in crystallizing assume the figure of a cube, the regular octohedron, or some form allied to it. Gold, silver, and copper occur naturally in crystals; while others crystallize when they pass gradually from the liquid to the solid condition. Crystals are most readily procured from those metals which fuse at a low temperature; and bismuth, from conducting heat less perfectly than other metals, and therefore cooling more slowly, is best fitted for the purpose. The process should be conducted in the way already described for forming crystals of sulphur.

Metals, with the exception of mercury, are solid at common temperatures; but they may all be liquefied by heat. The degree at which they *fuse*, or their *point* of *fusion*, is very different for different metals, as appears from the following table:—

Table of the Fusibility of different Metals.

		Fahr.	
Fusible below a red heat.	Mercury . .	—39°	Different chemists.
	Potassium . .	136	Gay-Lussac and Thenard.
	Sodium . .	190	
	Tin . .	442	Crichton.
	Bismuth . .	497	
	Lead . .	612	
	Tellurium—rather less fusible than lead		Klaproth.
	Arsenic—undetermined.		
	Zinc . . .	773	Daniell.
	Antimony—a little below a red heat.		
	Cadmium . about	442	Stromeyer.

Table of the Fusibility of different Metals—(continued).

Infusible below a red heat.	Silver	1873	Daniell.	
	Copper	1996		
	Gold	2016		
	Iron, cast	2786		
	Iron, malleable		Requiring the highest heat of a smith's forge.	
	Cobalt—rather less fusible than iron.			
	Manganese		Requiring the highest heat of a smith's forge.	
	Nickel—nearly the same as cobalt.			
	Palladium			
	Molybdenum		Almost infusible, and not to be procured in buttons by the heat of a smith's forge.	Fusible before the oxy-hydrogen blowpipe.
	Uranium			
	Tungsten			
	Chromium			
	Titanium		Infusible in the heat of a smith's forge, but fusible before the oxy-hydrogen blowpipe.	
	Cerium			
	Lantanium			
	Osmium			
	Iridium			
	Rhodium			
	Platinum			
	Columbium			

Metals differ also in volatility. Some are readily volatilized by heat, while others are of so fixed a nature that they may be exposed to the most intense heat of a wind furnace without being dissipated in vapour. There are seven metals, the volatility of which has been ascertained with certainty; namely, cadmium, mercury, arsenic, tellurium, potassium, sodium, and zinc.

Metals cannot be resolved into more simple parts; and therefore, in the present state of chemistry, they must be regarded as elementary bodies. It was formerly conceived that they might be converted into each other; and this notion led to the vain attempts of the alchemists to convert the baser metals into gold. The chemist has now learned that his art solely consists in resolving compound bodies into their elements, and causing substances to unite which were previously uncombined. One elementary principle cannot, so far as our experience goes, be made to assume the properties peculiar to another. Some attempts have recently been made, by Dr. Samuel Brown, to demonstrate, experimentally, the possibility of isomeric transmutation of elements, but without success. Dr. Brown announced, at one time, that he had transmuted iron into rhodium, but this statement has not been confirmed The subject of isomeric transmutation has been discussed in the section on Isomeric Bodies.

Metals have an extensive range of affinity, and on this account few of them are found in the earth *native*, that is, in an uncombined form. They commonly occur in combination with other bodies, especially with oxygen and sulphur, in which state they are said to be *mineralized*. It is a singular fact in the chemical history of the metals, that they are little disposed to combine in the metallic state with compound bodies, such as an oxide or an acid. They unite readily, on the contrary, with elementary substances. Thus they often combine with each other, yielding compounds termed *alloys*, which possess all the characteristic physical properties of pure metals. They unite likewise with the simple non-metallic substances, such as oxygen, chlorine, and sulphur, giving rise to new bodies in which the metallic character is wholly wanting. In all these combinations the same tendency to unite in a few definite proportions, is equally conspicuous as in that department of the science of which I have just completed the description, namely, that of the non-metallic bodies. The chemical changes are regulated by the same general laws, and in describing them the same nomenclature is applicable.

The order which it is proposed to follow in describing the metals has already been explained in the Introduction; but before treating of each separately, some general observations may be premised, by which the study of this subject will be much facilitated.

Metals are of a combustible nature, that is, they are not only susceptible of slow oxidation, but, under favourable circumstances, they unite rapidly with oxygen, giving rise to all the phenomena of real combustion. Zinc burns with a brilliant flame when heated to full redness in the open air; iron emits vivid scintillations on being inflamed in an atmosphere of oxygen gas; and the least oxidable metals, such as gold and platinum, scintillate in a similar manner when heated by the oxy-hydrogen blowpipe.

The product either of the slow or rapid oxidation of a metal, when heated in the air, has an earthy aspect, and was called a *calx* by the older chemists, the process of forming it being expressed by the term *calcination*. Another method of oxidizing metals is by *deflagration*; that is, by mixing them with nitrate or chlorate of potassa, and projecting the mixture into a red-hot crucible. Most metals may be oxidized by digestion in nitric acid; and nitro-hydrochloric acid is an oxidizing agent of still greater power.

Some metals unite with oxygen in one proportion only, but most of them have two or three degrees of oxidation. Metals differ remarkably in their relative forces of attraction for oxygen. Potassium and sodium, for example, are oxidized by mere exposure to the air; and they decompose water at all temperatures the instant they come in contact with it. Iron and copper may be preserved in dry air without change, nor can they decompose water at common temperatures; but they are both slowly oxidized by exposure to a moist atmosphere, and combine rapidly with oxygen when heated to redness in the open air. Iron has a stronger affinity for oxygen than copper; for the former decomposes water at a red heat, whereas the latter cannot produce that effect. Mercury is less disposed than copper to unite with oxygen. Thus it may be exposed without change to the influence of a moist atmosphere. At a temperature of 650° or 700° it is oxidized; but at a red heat it is reduced to the metallic state, while oxide of copper can sustain the strongest heat of a blast furnace without losing its oxygen. The affinity of gold for oxygen is still weaker than that of mercury; for it will bear the most intense heat of our furnaces without oxidation, and its oxide, when formed in another way, is decomposed by a heat below redness.

Metallic oxides suffer *reduction,* or may be reduced to the metallic state in several ways:

1. By heat alone. By this method the oxides of gold, silver, mercury, platinum, and all the other so-called noble metals, may be decomposed.

2. By the united agency of heat and combustible matter. Thus, by transmitting a current of hydrogen gas over the oxides of copper or iron heated to redness in a tube of porcelain, water is generated, and the metals are obtained in a pure form. Carbonaceous matters are likewise used for the purpose with great success. Potassa and soda, for example, may be decomposed by exposing them to a white heat after being intimately mixed with charcoal in fine powder. A similar process is employed in metallurgy for extracting metals from their ores, the inflammable materials being wood, charcoal, coke, or coal. In the more delicate operations of the laboratory, charcoal, black flux, formiate of soda, and especially cyanide of potassium, are preferred.

3. By the galvanic battery. This is a still more powerful agent than the preceding; since some oxides, such as baryta and strontia, which resist the united influence of heat and charcoal, are reduced by the agency of galvanism. It is by a peculiar arrangement for the reduction of metals by means of galvanism, that the beautiful invention of the electrotype, including the arts of electro-gilding and electro-plating, has been rendered available for practical purposes.

4. By the action of deoxidizing agents on metallic solutions. Phosphorous acid, for example, when added to a liquid containing oxide of mercury, deprives the oxide of its oxygen, metallic mercury subsides, and phosphoric acid is generated. Formic acid and formiate of soda, when boiled with the solutions of the oxides of gold, platinum, silver, mercury, &c., reduces the metals. In like manner, one metal may be precipitated by another, provided the affinity of the latter for oxygen exceed that of the former. Thus, when mercury is added to a solution of nitrate of the oxide of silver, metallic silver is thrown down,

and oxide of mercury is dissolved by the nitric acid. On placing metallic copper in the liquid, pure mercury subsides, and a nitrate of the oxide of copper is formed ; and from this solution metallic copper may be precipitated by means of iron.

Metals, like the simple non-metallic bodies, may give rise to oxides or acids by combining with oxygen. The former are the most frequent products. Many metals which are not acidified by oxygen may be formed into oxides ; whereas one metal only, arsenic, is capable of forming acids and not an oxide. All the other metals which are convertible into acids by oxygen, such as chromium, tungsten, and molybdenum, are also susceptible of yielding one or more oxides. In these instances, the acids always contain a larger quantity of oxygen than the oxides of the same metal.

Many of the metallic oxides have the property of combining with acids. In some instances all the oxides of a metal are capable of forming salts with acids, as is exemplified by the oxides of iron ; but, generally, the protoxide is the sole *alkaline* or *salifiable base*. Most of the metallic oxides are insoluble in water ; but all those that are soluble have the property of giving a brown stain to yellow turmeric paper, and of restoring the blue colour of reddened litmus.

Oxides sometimes unite with each other, and form definite compounds. The most abundant ore of chromium, commonly called chromate of iron, is an instance of this kind ; and the red oxide of manganese, the magnetic oxide of iron, and the red oxide of lead, appear to belong to the same class of bodies. It is to be observed, however, that in the three last cases it is two oxides of the same metal which unite to form the compound.

Chlorine has a powerful affinity for metallic substances. It combines readily with most metals at common temperatures, and the action is in many instances so violent as to be accompanied with the evolution of light. For example, when powdered zinc, arsenic, or antimony is thrown into a jar of chlorine gas, the metal is instantly inflamed. The attraction of chlorine for metals even surpasses that of oxygen. Thus, when chlorine is brought into contact at a red heat, with pure lime, magnesia, baryta, strontia, potassa, or soda, oxygen is emitted, and a chloride of the metal is generated, the elements of which are so strongly united that no temperature hitherto tried can separate them. All other metallic oxides are, with few exceptions, acted on in the same manner by chlorine, and in some cases the change takes place below the temperature of ignition.

Most of the metallic chlorides are solid at common temperatures.

They are fusible by heat, assume a crystalline texture in cooling, and under favourable circumstances crystallize with regularity. Several of them, such as the chlorides of tin, arsenic, antimony, and mercury, are volatile, and may be sublimed without change. They are for the most part colourless, do not possess the metallic lustre, and have the aspect of a salt. Two of the chlorides are insoluble in water, namely, chloride of silver and protochloride of mercury, while that of lead is very sparingly soluble. Several, such as the chlorides of antimony, arsenic, and titanium, are decomposed by that liquid; but most of them are more or less soluble.

Some of the metallic chlorides, those especially of gold and platinum, are decomposable by heat. All the chlorides of the common metals are decomposed at a red heat by hydrogen gas, hydrochloric acid being disengaged while the metal is set free. Pure charcoal does not effect their decomposition; but if moisture be present at the same time, hydrochloric and carbonic acid gases are formed, and the metal remains. They resist the action of anhydrous sulphuric acid; but all the chlorides, excepting those of silver and mercury, are readily decomposed by hydrated sulphuric acid, with disengagement of hydrochloric acid gas. The change is accompanied with decomposition of water, the hydrogen of which combines with chlorine, and its oxygen with the metal. When in solution, they may be recognized by yielding with nitrate of oxide of silver a white precipitate, which is chloride of silver.

Metallic chlorides may in most cases be formed by direct action of chlorine on the pure metals. They are also frequently procured by dissolving metallic oxides in hydrochloric acid, evaporating to dryness, and applying heat so long as any water is expelled. Metallic chlorides are often deposited from such solutions by crystallization. Chlorides are also formed by passing hydrochloric acid gas over the oxides in tubes heated to redness. The action of hydrochloric acid on oxides, whether in solution or in the dry way, is represented by the following formulæ; one of which applies to the case of protoxides, the other to that of sesquioxides. $MO + HCl = HO + MCl$; and $M_2O_3 + 3HCl = 3HO + M_2Cl_3$. Here M stands for any metal, and it will be seen that the chlorides correspond in composition with the oxides, so that for every eq. of oxygen in the oxide an eq. of hydrochloric acid is required.

Iodine has a strong attraction for metals; and most of the compounds which it forms with them sustain a red heat in close vessels without decomposition. But in the degree of its affinity for metallic substances it is inferior to chlorine and oxygen. We have seen that chlorine has a stronger affinity than oxygen for metals, since it decomposes nearly all oxides at high temperatures; and it separates iodine also from metals under the same circumstances. If the vapour of iodine is brought into contact with potassa, soda, protoxide of lead, or oxide of bismuth, heated to redness, oxygen gas is evolved, and the metals of those oxides will unite with iodine. But iodine, so far as is known, cannot separate oxygen from any other metal; nay, all the iodides, except those just mentioned, are decomposed by exposure to oxygen gas at the temperature of ignition. All the iodides are decomposed by chlorine, bromine, and concentrated sulphuric and nitric acids; and the iodine which is set free may be recognized either by the colour of its vapour, or by its action on starch. The metallic iodides are generated under circumstances analogous to those above mentioned for procuring the chlorides.

The action of iodine on metallic oxides, when dissolved or suspended in water, is precisely analogous to that of chlorine. On adding iodine to a solution of the pure alkalies or alkaline earths, an iodide and iodate are generated.

Bromine in its affinity for metallic substances is intermediate between chlorine and iodine; for while chlorine disengages bromine from its combination with metals, metallic iodides are decomposed by bromine. The same phenomena attend the union of bromine with metals, as accompany the formation of metallic chlorides. Thus, antimony and tin take fire by contact with bromine, and its action with potassium is attended with a flash of light, and intense heat. These compounds have as yet been but partially examined. They may be formed by the action of bromine on the pure metals, and often by dissolving metallic oxides in hydrobromic acid, and evaporating the solution to dryness. Bromine unites with potassa, soda, and some other oxides, constituting bleaching compounds similar to the chlorides above described. Bromide of lime is obtained by the action of bromine on milk of lime, a yellowish solution being formed with water, which bleaches powerfully.

As fluorine has not hitherto been obtained in a separate state, the nature of its action on the metals is unknown; but the chief difficulty of procuring it in an insulated form appears to arise from its extremely powerful affinity for metallic substances, in consequence of which, at the moment of becoming free, it attacks the vessels and instruments employed in its preparation. The best mode of preparing the soluble fluorides, such as those of potassium and sodium, is by dissolving the carbonates of these alkalies in hydrofluoric acid, and evaporating the solution to perfect dryness. The insoluble fluorides are easily formed by precipitation from the soluble fluorides. They are without exception decomposed by concentrated sulphuric acid with the aid of heat; and the hydrofluoric acid, in escaping, may easily be detected by its action on glass.

Sulphur, like the preceding elementary substances, has a strong tendency to unite with metals, and the combination may be effected in several ways:—

1. By heating the metal directly with sulphur. The metal, in the form of powder or filings, is mixed with a due proportion of sulphur, and the mixture heated in an earthern crucible, which is covered to prevent the access of air; or if the metal can sustain a red heat without fusing, the vapour of sulphur may be passed over it while heated to redness in a tube of porcelain. The act of combination, which frequently ensues below the temperature of ignition, is attended by free disengagement of heat, which in several instances is so great, that the whole mass becomes luminous, and shines with a vivid light. This appearance of combustion, which occurs quite independently of the presence of oxygen, is exemplified by the sulphurets of potassium, sodium, copper, iron, lead, and bismuth.

2. By igniting a mixture of a metallic oxide and sulphur.

3. By depriving the sulphate of an oxide of its oxygen by means of heat and combustible matter. Charcoal or hydrogen gas may be employed for the purpose, as will be described immediately.

4. By hydrosulphuric acid, or a soluble metallic sulphuret. Nearly all the salts of the second class of metals are decomposed when a current of hydrosulphuric acid gas is conducted into their solutions. The salts of uranium, iron, manganese, cobalt, and nickel are exceptions: but these are precipitated by sulphuret of potassium. The action of sulphuretted hydrogen (hydrosulphuric acid) on metallic oxides is analogous to that of hydrochloric acid above described, and is represented by the following formulæ for the respective cases of protoxides and sesquioxides, $MO + HS = HO + MS$; and $M_2O_3 + 3HS = 3HO + M_2S_3$.

The sulphurets are opaque brittle solids, many of which, such as the sulphurets of lead, antimony, and iron, have a metallic lustre. They are all fusible by heat, and commonly assume a crystalline texture in cooling. Most of them are fixed in the fire; but the sulphurets of mercury and arsenic are remarkable for their volatility. All the sulphurets, excepting those of the first class of metals, are insoluble in water.

Most of the protosulphurets support an intense heat without decomposition; but, in general, those which contain more than one equivalent of sulphur, lose part of it when strongly heated. They are all decomposed without exception by exposure to the combined agency of air or oxygen gas and heat; and the products depend entirely on the degree of heat and the nature of the metal. The sulphuret is more or less converted into the sulphate of an oxide, provided the sulphate is able to support the temperature employed in the operation. If this is not the case, the sulphur is evolved under the form of sulphurous acid, and a metallic oxide is left; or if the oxide itself is decomposed by heat, the pure metal remains. The action of heat and air in decomposing metallic sulphurets is the basis of several metallurgic processes. A few sulphurets are decomposed by the action of hydrogen gas at a red heat, the pure metal being set free and hydrosulphuric acid evolved. Rose finds that the only sulphurets which admit of being easily reduced to the metallic state in this way are those of antimony, bismuth, and silver. The sulphuret of tin is decomposed with difficulty, and requires a very high temperature. All the other sulphurets which he subjected to this treatment were either deprived of a part only of their sulphur, such as bisulphuret of iron, or were not attacked at all, as happened with the sulphurets of zinc, lead, and copper. (Poggendorff's Annalen, iv. 109.)

Many of the metallic sulphurets were formerly thought to be compounds of sulphur and a metallic oxide; an error first pointed out by Proust, who demonstrated that protosulphuret of iron, as well as the bisulphuret, are compounds of sulphur and metallic iron without any oxygen. (Journal de Physique, liii.) He proved the same of the sulphurets of other metals, such as mercury and copper. He was of opinion, however, that in some instances sulphur does unite with a metallic oxide. Thus, when sulphur and peroxide of tin are heated together, sulphurous acid is disengaged, and the residue according to Proust is a sulphuret of the protoxide, but in this he was in error.

In 1817 Vauquelin extended these views to the compounds formed by heating an alkali or an alkaline earth with sulphur, which were previously regarded as sulphurets of a metallic oxide. He explained that the elements of the alkali unite with separate portions of sulphur, forming a metallic sulphuret and sulphuric acid, the latter of which unites with undecomposed alkali. Thus, in preparing the so-called *liver of sulphur*, made by fusing carbonate of potassa with sulphur, one portion of the alkali is completely decomposed, its elements unite separately with sulphur, giving rise to sulphuret of potassium and sulphuric acid, the latter of which combines with undecomposed potassa.

Those views were at the same time supported by Gay-Lussac. (An. de Ch. et Ph. vi.)

One of the chief arguments adduced by Vauquelin in support of his opinion was drawn from the action of charcoal on sulphate of potassa. When a mixture of this salt with powdered charcoal is ignited without exposure to the air, carbonic oxide and carbonic acid gases are formed, and a sulphuret is left, analogous both in appearance and properties to that which may be made by igniting carbonate of potassa directly with sulphur. They are both essentially the same substance, and Vauquelin conceived from the strong attraction of carbon for oxygen, that both the sulphuric acid and potassa would be decomposed by charcoal at a high temperature; and that, consequently, the product must be a sulphuret of potassium.

Berthier has proved that these changes do actually occur. (An. de Ch. et Ph. xxii.) He put a known weight of sulphate of baryta into a crucible lined with a mixture of clay and charcoal, defended it from contact with the air, and exposed it to a white heat for the space of two hours. By this treatment it suffered complete decomposition, and it was found that in passing into a sulphuret, it had suffered a loss in weight precisely equal to the quantity of oxygen originally contained in the acid and earth. This circumstance, coupled with the fact that there had been no loss of sulphur, is decisive evidence that the baryta as well as the acid had lost its oxygen, and that a sulphuret of barium had been formed. He obtained the same results also with the sulphates of strontia, lime, potassa, and soda; but from the easy fusibility of the sulphurets of potassium and sodium, their loss of weight could not be determined with such precision as in the other instances.

The experiments of Berzelius, performed about the same time, are exceedingly elegant, and still more satisfactory than the foregoing. (An. de Ch. et Ph. xx.) He transmitted a current of dry hydrogen gas over a known quantity of sulphate of potassa, heated to redness. It was expected from the strong affinity of hydrogen for oxygen, that the sulphate would be decomposed; and, accordingly, a considerable quantity of water was formed, which was carefully collected and weighed. The loss of weight which the salt had experienced was precisely equivalent to the oxygen of the acid and alkali; and the oxygen of the water was exactly equal to the loss in weight. A similar result was obtained with the sulphates of soda, baryta, strontia, and lime.

It is demonstrated, therefore, that the metallic bases of the alkalies and alkaline earths agree with the common metals in their disposition to unite with sulphur. It is now certain that, whether a sulphate be decomposed by hydrogen or charcoal, or sulphur ignited with an alkali or an alkaline earth, a metallic sulphuret is always the product. Direct combination between sulphur and a metallic oxide is a very rare occurrence, nor has the existence of such a compound been clearly established. Gay-Lussac indeed states that, when an alkali or an alkaline earth is heated with sulphur in such a manner that the temperature is never so high as a low red heat, the product is really the sulphuret of an oxide. But the facts adduced in favour of this opinion are not altogether satisfactory, so that the real nature of the product must be decided by future observation.

Several of the metallic sulphurets occur abundantly in nature. Those that are most frequently met with are the sulphurets of lead, antimony, copper, iron, zinc, molybdenum, and silver.

The metallic seleniurets have so close a resemblance in their chemical relations to the sulphurets, that it is unnecessary to give a separate description of them. They may be prepared either by bringing selenium in contact with the metals at a high temperature, or by the action of hydroselenic acid on metallic solutions.

Respecting the preceding compounds there remains one subject, the consideration of which, as applying equally to all, has been purposely delayed. The non-metallic ingredient of each is the radical of a hydracid, that is, has the property of forming with hydrogen an acid, which, like other acids, is unable to unite with metals, but appears to combine readily with many metallic oxides. Owing to this circumstance, a difficulty arises in explaining the action of such substances on water. Thus, when chloride of potassium is put into water, it may dissolve without suffering any other chemical change, and the liquid accordingly contain chloride of potassium in solution. But it is also possible that the elements of this compound may react on those of water, its potassium uniting with oxygen, and its chlorine with hydrogen; and as the resulting potassa and hydrochloric acid have a strong affinity for each other, the solution would of course contain hydrochlorate of potassa. A similar uncertainty attends the action of water on other metallic chlorides, and on the compounds of metals with iodine, bromine, sulphur, and similar substances; so that when iodide, sulphuret, and cyanuret of potassium are put into water, it may be doubted whether they dissolve as such, or whether they may not be converted, by decomposition of water, into hydriodate, hydrosulphate, and hydrocyanate of potassa. This question would at once be decided, could it be ascertained whether water is or is not decomposed during the process of solution; but this is the precise point of difficulty, since, from the operation of the laws of chemical union, no disengagement of gas does or can take place by which the occurrence of such a change may be indicated. Chemists, acocrdingly, being guided by probabilities, are divided in opinion, and I shall therefore give a brief statement of both views, with the arguments in favour of each.

According to one view, then, chloride of potassium and all similar compounds dissolve in water without undergoing any other change, and are deposited in their original state by crystallization. When any hydracid, such as hydrochloric or hydriodic acid, is mixed with potassa or any similar metallic oxide, the acid and salifiable base do not unite, but the oxygen of the oxide combines with the hydrogen of the acid, and the metal itself with the radical of the hydracid. This kind of double decomposition unquestionably takes place in some instances, as when hydrosulphuric acid acts upon acetate of oxide of lead, the insoluble sulphuret of lead being actually precipitated; but it is also thought to occur even when the transparency of the solution is undisturbed. It is argued, accordingly, that hydrochlorate of potassa, and the salts of the hydracids in general, have no existence. Thus, when nitrate of the oxide of silver is added to a solution of chloride of potassium, metallic silver is said to unite with chlorine, while the oxygen of the oxide of silver combines with potassium; so that nitrate of potassa and chloride of silver are generated. On adding sulphuric acid to a solution of chloride of potassium, hydrochloric acid and potassa, not previously existing, are instantly formed in consequence of the decomposition of water, which yields its hydrogen to chlorine, and its oxygen to potassium; exactly as happens when concentrated sulphuric acid is brought into contact with solid chloride of potassium. It is further believed that the crystallized hydrochlorate of lime, baryta, and strontia, which contain water or its elements, are metallic chlorides combined with water of crystallization; and the same view is applied to all analogous compounds.

According to the other doctrine, chloride of potassium is converted into hydrochlorate of potassa in the act of dissolving; and when the solution is evaporated, the elements existing in the salt reunite at the moment of crystallization, and crystals of chloride of potassium are deposited. The same explanation applies in all cases, when the salt of a hydracid crystallizes without retaining the elements of water. Of those compounds which in crystallizing retain water or its elements in combination, two opinions may be formed. Thus crystallized hydrochlorate of baryta, which consists of one equivalent of chlorine, one of barium, two of oxygen, and two of hydrogen, may be regarded as a compound either of hydrochlorate of baryta with one equivalent of water of crystallization, or of chloride of barium with two equivalents of water.

When exposed to heat, two equivalents of water are expelled, and chloride of barium is left. When nitrate of the oxide of silver is mixed in solution with hydrochlorate of potassa, the oxygen of the oxide of silver unites with the hydrogen of the hydrochloric acid, chloride of silver is precipitated, and nitrate of potassa remains in the liquid. On adding sulphuric acid to a hydrochlorate, hydrochloric acid is simply displaced, just as when carbonic acid in marble is separated from lime by the action of nitric acid.

On comparing these opinions, it is manifest that both are consistent with well-known affinities. When a metallic chloride is dissolved in water, the attraction of chlorine for the metal, and that of oxygen for hydrogen, tend to prevent chemical change; but the affinities of the metal for oxygen, of chlorine for hydrogen, and of hydrochloric acid for metallic oxides, co-operate towards determining the decomposition of water, and the production of a hydrochlorate. In favour of the latter change as actually taking place, the following considerations may be adduced :—1. The solution of some compounds, such as sulphuret of potassium, actually emit an odour of hydrosulphuric acid. 2. Other compounds, such as the chlorides of copper, cobalt, and nickel, instantly acquire, when put into water, the colour peculiar to the salts of the oxides of those metals. 3. The solution of protochloride of iron, like the protosulphate, absorbs oxygen from the atmosphere; an effect which seems to indicate the presence of the protoxide of iron in the liquid. 4. In some instances there is direct proof of decomposition of water. Thus when sulphuret of aluminium is put into that fluid, alumina is generated, and hydrosulphuric acid gas disengaged with effervescence. In like manner chloride and sulphuret of silicon are converted by water into silica and hydrochloric and hydrosulphuric acid. In these cases the want of affinity between the new compounds causes their separation, and thus affords direct proof that water is decomposed. But the affinities which produce this change do not appear so likely to be effective, as those which are in operation when chloride of potassium is put into water; especially when it is considered that the attraction of chlorine for hydrogen, and potassium for oxygen, is aided by that of the resulting acid and oxide for each other.

These arguments may be successively answered in the following manner :—1. That solutions of cyanuret and sulphuret of potassium smell of hydrocyanic and hydrosulphuric acids, because the carbonic acid of the atmosphere gradually decomposes them. 2. That metals may yield with chlorine compounds of the same colour as the oxides of the same metals. Thus the terchloride and terfluoride of chromium have a red colour closely resembling that of chromic acid. 3. Protochloride of iron may attract oxygen from the air because of its known tendency to pass into the state of a sesquichloride, a portion of iron being at the same time converted into peroxide. 4. That while certain chlorides do really decompose water, it must be conceded that others dissolve directly without change. The bichloride of platinum and terchloride of gold are soluble in ether, forming solutions which must be regarded as chlorides and not hydrochlorates, since pure ether is anhydrous; and when aqueous solutions of these chlorides are agitated with ether, ethereal solutions of platinum and gold are formed, exactly similar to those made with ether alone. It can scarcely be doubted, then, that these chlorides exist as such in water. In favour of the same view it may with truth be alleged, that the chlorides of potassium and sodium dissolve in and crystallize out of water without evincing the least sign of any other change than mere solution and mere crystallization. Again, crystals of the so-called hydrochlorate of baryta become chloride of barium with loss of water by mere exposure to a dry air; a cause apparently inadequate to determine the hydrogen of the acid to unite with the oxygen of the oxide, but sufficient to explain the phenomena if the crystals were chloride of barium with water of crystallization.

On weighing these and other considerations of a like kind, it appears undeniable that *some* metallic chlorides, iodides, and similar compounds dissolve as such in water: that all do so, is a position which cannot, I think, be maintained; and therefore the existence of such compounds as hydracids united with metallic oxides, can scarcely be denied; and in the case of chloride of aluminium, which cannot be recovered from its solution in water, but yields alumina and hydrochloric acid, the change is obvious to the senses. At the same time it is necessary, to avoid a perpetually recurring two-fold explanation, to adhere consistently to one view; and the reader may have observed that I have, in this edition, uniformly gone on the supposition that chlorides, and the same class of bodies, dissolve as such in water. The considerations which have led to this preference are principally drawn from the history of the sulphur-salts.

Chemists are acquainted with several metallic phosphurets; and it is probable that phosphorus, like sulphur, is capable of uniting with all the metals. Little attention, however, has hitherto been devoted to their compounds; and for the greater part of our knowledge concerning them we are indebted to the researches of Pelletier and Rose. (An. de Ch. i. and xiii.; and Pog. An. vi. 205.)

The metallic phosphurets may be prepared in several ways. The most direct method is by bringing phosphorus in contact with metals at a high temperature, or by igniting metals in contact with phosphoric acid and charcoal. Several of the phosphurets may be formed by transmitting a current of phosphuretted hydrogen gas over metallic oxides heated to redness in a porcelain tube, when water is generated, and a phosphuret of the metal remains. By similar treatment the chlorides and sulphurets of many metals may be decomposed, and phosphurets formed, provided the metal is capable of retaining phosphorus at a red heat. According to Rose, the phosphurets of copper, nickel, cobalt, and iron are the only ones which admit of being advantageously prepared by this method. When chlorides are employed, hydrochloric acid, and with sulphurets hydrosulphuric acid gas, is of course generated.

Phosphorus is said to unite with metallic oxides. For example, phosphuret of lime is said to be formed by conducting the vapour of phosphorus over that earth at a low red heat; but it is probable that in this instance, as with a mixture of sulphur and an alkali, part of the metallic oxide is decomposed, and that the product contains phosphuret of calcium and phosphate of lime.

The only metallic carburets of importance are those of iron, which will be described in the section on that metal.

Hydrogen unites with few metals. The only metallic hydrogurets, or hydurets, known are those of zinc, potassium, arsenic, antimony, and tellurium.

Of late years several compounds of metals with nitrogen have been obtained: the nitrurets of copper, chromium, and mercury have alone been described. They are obtained with some difficulty, and are dark powders of a very explosive nature. They will be mentioned more particularly under the individual metals.

The discoveries of modern chemistry have materially added to the number of the metals, especially by associating with them a class of bodies which was formerly believed to be of a nature entirely different. The metallic bases of the alkalies and earths, previous to the year 1807, were altogether unknown; and before that date the list of metals, with few exceptions, included those only which are commonly employed in the arts, and which are hence often called the common metals. In consequence of this increase in number, it is found convenient, for the purpose of description, to arrange them in separate groups; and as the alkalies and earths differ in several respects from the oxides of other metals, it will be convenient to describe them separately. I have accordingly divided the metals into the two following classes:—

Class I. Metals which by oxidation yield alkalies and earths.

Class II. Metals, the oxides of which are neither alkalies nor earths.

Class I. This class includes 12 metals, which may properly be arranged in three orders.

Order I. Metallic bases of the alkalies. They are three in number; namely,

Potassium, Sodium, Lithium.

These metals have such a powerful attraction for oxygen, that they decompose cold water and even ice at the moment of contact, and are oxidized with disengagement of hydrogen gas. The resulting oxides are distinguished by their causticity and solubility in water, and by possessing alkaline properties in an eminent degree.

They are called *alkalies*, and their metallic bases are sometimes termed *alkaline* or *alkaligenous* metals.

Order 2. Metallic bases of the alkaline earths. These are four in number; namely,

Barium, Strontium, Calcium, Magnesium.

These metals, excepting magnesium, also decompose water rapidly at common temperatures. The resulting oxides are called *alkaline earths;* because, while in their appearance they resemble the earths, they are similar to the alkalies in having a strong alkaline reaction with test paper, and in neutralizing acids. The first three are strongly caustic, and baryta and strontia are soluble in water to a considerable extent.

Order 3. Metallic bases of the earths. These are five in number; namely,

Aluminium, Glucinium, Yttrium.
Thorium, Zirconium,

The oxides of these metals are well known as the pure earths. They are white and of an earthy appearance, in their ordinary state are quite insoluble in water, and do not affect the colour of turmeric or litmus paper. As salifiable bases they are inferior to the alkaline earths. Erbium and terbium may possibly be hereafter added to this order.

Class II. The number of the metals included in this class amounts to upwards of 30. They are all capable of uniting with oxygen, and generally in more than one proportion. Their protoxides have an earthy appearance, but with few exceptions are coloured. They are insoluble in water, and in general do not affect the colour of test paper.

Most of them act as salifiable bases in uniting with acids, and forming salts; but in this respect they are much inferior to the alkalies and alkaline earths, by which they may be separated from their combinations. Several of these metals are capable of forming with oxygen, compounds which possess the characters of acids. The metals in which this property has been noticed are, manganese, arsenic, chromium, vanadium, molybdenum, tungsten, antimony, columbium, titanium, tellurium, gold, and osmium.

The metals belonging to the second class may be conveniently arranged in the three following orders:—

Order 1. Metals which decompose water at a red heat. They are seven in number; namely,

Manganese,
Zinc,
Iron,
Tin,
Cadmium,
Cobalt,
Nickel.

Order 2. Metals which do not decompose water at at any temperature, and the oxides of which are not reduced to the metallic state by the sole action of heat. They are fifteen in number; namely,

Arsenic,
Chromium,
Vanadium,
Molybdenum,
Tungsten,
Columbium,
Pelopium,
Niobium,
Antimony,
Uranium,
Cerium,
Lantanium,
Didymium,
Erbium,
Terbium,
Bismuth,
Titanium,
Tellurium,
Copper,
Lead.

Order 3. Metals, the oxides of which are decomposed by a red heat. These are,

Mercury,
Silver,
Gold,
Platinum,
Palladium,
Rhodium,
Osmium,
Iridium,
Ruthenium.

CLASS I.

METALS WHICH BY OXIDATION YIELD ALKALIES OR EARTHS.

ORDER I.

METALLIC BASES OF THE ALKALIES.

SECTION I.

POTASSIUM.

Hist. and Prep.—Discovered in the year 1807 by Davy, and the circumstances which led to the discovery have already been described. Hydrate of potassa, slightly moistened for the purpose of increasing its conducting power, was made to communicate with the opposite poles of a galvanic battery of 200 double plates; when the oxygen both of the water and the potassa passed over to the positive pole, while the hydrogen of the former, and the potassium of the latter, made their appearance at the negative pole. By this process potassium is obtained in small quantity only; but Gay-Lussac and Thenard invented a method by which a more abundant supply may be procured. (Recherches Physico-Chimiques, vol. i.) Their process consists in bringing fused hydrate of potassa in contact with turnings of iron heated to whiteness in a gun-barrel. The iron, under these circumstances, deprives the water and potassa of oxygen, hydrogen gas combined with a little potassium is evolved, and pure potassium sublimes, and may be collected in a cool part of the apparatus.

Potassium may also be prepared, as first noticed by Curaudau, by mixing dry carbonate of potassa with half its weight of powdered charcoal, and exposing the mixture, contained in a gun-barrel or spheroidal iron bottle, to a strong heat. An improvement on both processes has been made by Brunner, who decomposes potassa by means of iron and charcoal. From eight ounces of fused carbonate of potassa, six ounces of iron filings, and two ounces of charcoal, mixed intimately and heated in an iron bottle, he obtained 140 grains of potassium. (Quarterly Journal, xv. 379.) Berzelius has observed that the potassium thus made, though fit for all the usual purposes to which it is applied, contains a minute quantity of carbon; and therefore, if required to be quite pure, must be rendered so by distillation in a retort of iron or green glass. A modification of this process has been since described by Wöhler, who effects the decomposition of the potassa solely by means of charcoal. The material employed for the purpose is carbonate of potassa prepared by heating cream of tartar to redness in a covered crucible. (Poggendorff's Annalen, iv. 23.) According to Liebig, 2 eq. of charcoal and 1 eq. of carbonate of potassa react on each other, and form 1 eq. of potassium and 3 eq. of carbonic oxide; or

$$\begin{matrix} \mathrm{KO} + \mathrm{CO_2} \\ \text{and } 2\mathrm{C} \end{matrix} \ \text{yield} \ \begin{matrix} \mathrm{K} \\ \text{and } 3\mathrm{CO}. \end{matrix}$$

The whole of the potassium thus liberated is not, however, obtained in the metallic form, for 3 out of every 4 eq. combine with 7 out of the 12 eq. of carbonic oxide gas at the same time produced. The resulting compound has a dark grey colour, and is recognised by burning on water with a violent flame, and the production of croconate and oxalate of potassa. This compound is sometimes almost the sole product of the process. (Geiger's Pharmacie, 348.)

Prop.—Solid at the ordinary temperature of the atmosphere. At 70° it is somewhat fluid, though its fluidity is not perfect till it is heated to 150°. At 50° it is soft and malleable, and yields like wax to the pressure of the fingers; but it becomes brittle when cooled to 32°. It sublimes at a low red heat without undergoing any change, provided atmospheric air be completely excluded. Its texture is crystalline, as may be seen by breaking it across while brittle, and cubic crystals have been obtained by Pleischl. (Pog. An. xxxi. 431.) In colour and lustre it is precisely similar to mercury. At 60° its density is 0·865, so that it is considerably lighter than water. It is quite opaque, and is a good conductor of heat and electricity.

The most prominent chemical property of potassium is its affinity for oxygen. It oxidizes rapidly in the air, or by contact with fluids which contain oxygen. On this account it must be preserved either in glass tubes hermetically sealed, or under the surface of liquids, such as naphtha, of which oxygen is not an element. If heated in the open air, it takes fire, and burns with a purple flame and great evolution of heat. It decomposes water on the instant of touching it; and so much heat is disengaged, that the potassium is inflamed, and burns vividly while swimming upon its surface. The hydrogen unites with a little potassium at the moment of separation; and this compound takes fire as it escapes, and thus augments the brilliancy of the combustion. When potassium is plunged under water, violent reaction ensues, with the production of a red heat, but without flame, and pure hydrogen gas is evolved.

The combining weight or equivalent of potassium is easily deducible from the composition of potassa and chloride of potassium, which are admitted to consist of single equivalents of their elements. Gay-Lussac and Thenard, and Davy, inferred the composition of potassa from the hydrogen gas evolved when a known weight of potassium is oxidized under water, the volume of the oxygen which unites with the metal being equal to half the volume of the hydrogen. Berzelius analyzed chloride of potassium by means of nitrate of oxide of silver, and inferred that 39·15 is the eq. of potassium. Its symb. is K. The following compounds of potassium are described in this section:—

	Potassium.			Equiv.	Formulæ.
Protoxide .	39·15	1 eq.+Oxygen	8	1 eq.= 47·15	$K+O$ or KO.
Peroxide . .	39·15	1 eq.+ „	24	3 eq.= 63·15	$K+3O$ or KO_3.
Chloride . .	39·15	1 eq.+Chlor.	35·42	1 eq.= 74·57	$K+Cl$ or KCl.
Iodide . .	39·15	1 eq.+Iodine	126·3	1 eq.=165·45	$K+I$ or KI.
Bromide . .	39·15	1 eq.+Brom.	78·4	1 eq.=117·55	$K+Br$ or KBr.
Fluoride . .	39·15	1 eq.+Fluor.	18·68	1 eq.= 57·83	$K+F$ or KF.
Hydurets . .	Composition uncertain.				
Carburet . .					
Sulphuret .	39·15	1 eq.+Sulphur	16·1	1 eq.= 55·25	$K+S$ or KS.
Bisulphuret .	39·15	1 eq.+do.	32·2	2 eq.= 71·35	$K+2S$ or KS_2.
Tersulphuret .	39·15	1 eq.+do.	48·3	3 eq.= 87·45	$K+3S$ or KS_3.
Quadrosulphuret	39·15	1 eq.+do.	64·4	4 eq.=103·35	$K+4S$ or KS_4.
Quintosulphuret	39·15	1 eq.+do.	80·5	5 eq.=119·65	$K+5S$ or KS_5.
Phosphurets .	Composition and number uncertain.				
Seleniurets .					

Protoxide of Potassium.—Hist. and Prep.—This compound, commonly called *potash* or *potassa*, and by the Germans *kali* (an Arabic word), is always formed when potassium is put into water, or when it is exposed at common temperatures to dry air or oxygen gas. By the former method the protoxide is obtained in combination with water; and in the latter it is anhydrous. In performing the last-mentioned process, the potassium should be cut into very thin slices; for otherwise the oxidation is incomplete. The product, when partially oxidized, is regarded by Berzelius as a distinct oxide; but most chemists admit it to be a mere mixture of potassa and potassium.

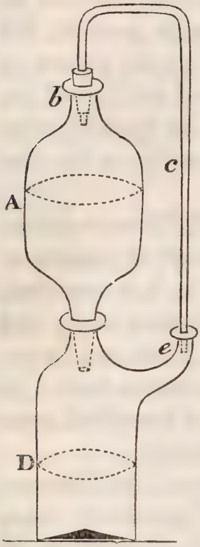
Prop.—Anhydrous potassa is a white solid substance, highly caustic, which fuses at a temperature somewhat above that of redness, and bears the strongest heat of a wind furnace without being decomposed or volatilized. It has a powerful affinity for water, and intense heat is disengaged during the act of combination. Three compounds are known; they are composed of 47·15, or 1 eq. of potassa united with 9, 27, and 45 parts, or 1, 3, and 5 eq. of water respectively. In the last compound a portion of the water probably exists as water of crystallization.

The protohydrate of potassa is solid at common temperatures. It fuses at a heat rather below redness, and assumes a somewhat crystalline texture in cooling. It is not decomposed by any degree of heat to which it has been exposed, and hence was long considered to be pure potassa. Its sp. gr. = 1·706. It is highly deliquescent, and requires about half its weight of water for solution. It is soluble, likewise, in alcohol. It destroys all animal textures, and on this account is employed in surgery as a caustic. It was formerly called *lapis causticus*, but it is now termed *potassa* and *potassa fusa* by the Colleges of Edinburgh and London. This preparation is made by evaporating the aqueous solution of potassa in a silver or clean iron capsule to the consistence of oil, and then pouring it into moulds. In this state it is impure, containing oxide of iron, together with chloride of potassium, and carbonate and sulphate of potassa. It is purified from these substances by solution in alcohol, and evaporation to the same extent as before in a silver vessel. The operation should be performed expeditiously, in order to prevent, as far as possible, the absorption of carbonic acid. When the common caustic potassa of the druggists is dissolved in water, a number of small bubbles of gas is disengaged, which is pure oxygen. Graham finds its quantity to be variable in different specimens, and to depend apparently on the impurity of the specimen.

If the protohydrate be exposed to the air, it rapidly becomes moist; but after absorbing a certain portion of water, a perfectly dry substance is again obtained, which is the terhydrate of potassa. It is very similar in all its characters to the protohydrate, but is much whiter and more crystalline in its texture. The quintohydrate is obtained by exposing a very concentrated solution of potassa to an intense cold. It is then deposited in four-sided prisms terminated by a four-sided pyramid, and sometimes in four-sided tables and octohedrons.

The aqueous solution of potassa, *aqua potassæ* of the Pharmacopœia, is prepared by decomposing carbonate of potassa by lime. The best proportions are 1 part of dry lime to 2 of carbonate of patassa. The lime is to be slaked by being covered with boiling water, when it forms a very minutely divided hydrate, in the form of a cream, every particle of which acts, which is not the case in dry slaking (Mohr). The carbonate is now dissolved in not less than 10 parts of hot water, and the cream of lime is added by small portions to the solution, and the mixture boiled after each addition in a clean iron vessel. The lime takes the carbonic acid, forming insoluble carbonate of lime. When the whole lime has been added, and the mixture has been boiled for some time, it is allowed to subside in the covered vessel, and the solution of caustic potassa may be decanted perfectly clear. If the carbonate have been pure, the solution yields by rapid evaporation pure hydrate of potassa. But if pearlash be employed, the sulphate of potash contained in it may be got rid of by evaporating till crystals appear; on cooling, the sulphate is so completely deposited that its presence can no longer be detected in the liquid. (Liebig.) The same chemist finds that a strong solution of caustic potassa actually deprives carbonate of lime of its acid, and that, from this circumstance, carbonate of potassa cannot be rendered quite caustic by lime unless diluted with about ten times its weight of water.

As pure potassa absorbs carbonic acid rapidly when freely exposed to the atmosphere, it is desirable to filter its solution in vessels containing as small a quantity of air as possible. This is easily effected by means of the filtering apparatus devised by Donovan. It consists of two vessels A and D, of equal capacity, and connected with each other as represented in the annexed wood-cut. The neck *b* of the upper vessel contains a tight cork, perforated to admit one end of the glass tube *c;* and the lower extremity of the same vessel terminates in a funnel pipe, which fits into one of the necks of the under vessel D by grinding, luting, or a tight cork. The vessel D is furnished with another neck *e*, which receives the lower end of the tube *c*, the junction being secured by means of a perforated cork, or luting. The throat of the funnel pipe is obstructed by a piece of coarse linen loosely rolled up, and not pressed down into the pipe itself. The solution is then poured in through the mouth at *b*, the cork and tube having been removed; and the first droppings, which are turbid, are not received into the lower vessel. The parts of the apparatus are next joined together, and the filtration may proceed at the slowest rate, without exposure to more air than was contained in the vessels at the beginning of the process. This apparatus should be made of green in preference to white glass, as the pure alkalies act on the former much less than on the latter. (Annals of Philosophy, xxvi. 115.)



The mode by which this apparatus acts scarcely needs explanation. In order that the liquid should descend freely, two conditions are required:—first, that the air above the liquid should have the same elastic force, and therefore exert the same pressure, as that below; and, secondly, as one means of securing the first condition, that the air should have free egress from the lower vessel. Both objects, it is manifest, are accomplished in the filtering apparatus of Donovan;

since for every drop of liquid which descends from the upper to the lower vessel, a corresponding portion of air passes along the tube *c* from the lower vessel to the upper. This apparatus is applicable to any other case where it is wished to exclude the atmosphere. Other similar contrivances will be found in the scientific journals, for which there is no space in this work.

Solution of potassa is highly caustic, and its taste intensely acrid. It possesses alkaline properties in an eminent degree, converting the vegetable blue colours to green, and neutralizing the strongest acids. It absorbs carbonic acid gas rapidly, and is consequently employed for withdrawing that substance from gaseous mixtures. When of the sp. gr. 1·25, it is used in the analysis of organic bodies, to absorb the carbonic acid formed, the weight of which is equal to the increase in the weight of the potash apparatus. The solution made from pearlash, which has deposited the sulphate of potash, is exactly of the proper strength for this purpose. (Gregory.) For the same reason it should be preserved in well-closed bottles, that it may not absorb carbonic acid from the atmosphere.

Potassa is employed as a reagent in detecting the presence of bodies, and in separating them from each other. The solid hydrate, owing to its strong affinity for water, is used for depriving gases of hygrometric moisture, and is admirably fitted for forming frigorific mixtures.

Potassa may be distinguished from all other substances by the following characters:—1. If tartaric acid be added in excess to a salt of potassa dissolved in cold water, and the solution be stirred with a glass rod, a white precipitate, bitartrate of potassa, soon appears, which forms peculiar white streaks upon the glass by the pressure of the rod in stirring 2. It is precipitated by perchloric acid in the cold, the perchlorate of potassa having nearly the same degree of solubility as the bitartrate. 3. A solution of chloride of platinum causes a yellow precipitate, the double chloride of platinum and potassium. A drop or two of hydrochloric acid should be added at the same time as the test, the mixture be evaporated to dryness at 212°, and a little cold water be afterwards added, when the double chloride is left in the form of small shining yellow crystals. Chloride of platinum dissolved in alcohol often gives an immediate precipitate, which falls of a pale yellow colour. 4. The alcoholic solution of carbazotic acid throws down potassa in yellow crystals of carbazotate of potassa, which is very sparingly soluble. 5. It yields a light gelatinous precipitate, the double fluoride of potassium and silicon, with silicated hydrofluoric acid. Of these tests carbazotic acid is the most delicate in a solution of pure potassa; but when the alkali is combined with a strong acid, the chloride of platinum is preferable.

The following test has been recommended by Harkort for distinguishing between potassa and soda in minerals:—Oxide of nickel, when fused by the blowpipe flame with borax, gives a brown glass; and this glass, if melted with a mineral containing potassa, becomes blue, an effect which is not produced by the presence of soda.

Its eq. is 47·15; symb. $K + O$, $\dot{K}$, or KO.

Peroxide.—When potassium burns in the open air or in oxygen gas, it is converted into an orange-coloured substance, which is peroxide of potassium. It may likewise be formed by conducting oxygen gas over potash at a red heat; and it is produced in small quantity when potash is heated in the open air. It is the residue of the decomposition of nitre by heat in metallic vessels, provided the temperature be kept up for a sufficient time. When the peroxide is put into water, it is resolved into oxygen and potash, the former of which escapes with effervescence, and the latter is dissolved. Its eq. is 63·15; symb. $K + 3O$, $\dddot{K}$, or KO_3.

Chloride of Potassium.—Potassium takes fire spontaneously in an atmosphere of chlorine, and burns with greater brilliancy than in oxygen gas. This chloride is generated with evolution of hydrogen when potassium is heated in hydrochloric acid gas; and it is the residue after the decomposition of chlorate of potassa by heat. It is formed when potassa is dissolved in a solution of hydrochloric acid, and is deposited by slow evaporation in anhydrous colourless cubic crystals. It has a saline and rather bitter taste, is insoluble in alcohol, and requires for solution 3 parts of water at 60°, and still less of hot water. Its eq. is 74·57; symb. $K + Cl$, or KCl.

Iodide of Potassium.—Prep.—This compound is formed with evolution of heat and light, when potassium is heated in contact with iodine; it is the sole residue after decomposing iodate of potassa by heat; and by neutralizing potassa with hydriodic acid it is obtained in solution. The simplest process for preparing it in quantity is to add iodine to a hot solution of pure potassa until the alkali is neutralized, which is known by the liquid assuming a permanent brown colour, when iodine of potassium and iodate of potassa are generated, to evaporate to dryness, and expose the dry mass in a platinum crucible to a gentle red heat in order to decompose the iodate. The fused mass is then dissolved out by water and crystallized. (Gregory, Edin. Med. and Surg. Jour., 1830.) Another process is to digest iodine with zinc or iron filings in water, and then decompose the resulting iodide of zinc or iron by a quantity of potassa just sufficient to precipitate the oxide.

Prop.—Iodide of potassium fuses readily when heated, and rises in vapour at a heat below full redness, especially in an open vessel. It is very soluble in water, requiring only two-thirds of its weight at 60° for solution, and in a moist atmosphere deliquesces. It dissolves also in strong alcohol, even in the cold; and the solution, when evaporated, yields colourless cubic crystals of iodide of potassium.

The commercial iodide is frequently impure, often containing chloride of potassium or sodium, and sulphate or carbonate of potassa, the last sometimes in very large quantity. It is well to purchase it in crystals, which ought not to deliquesce in a moderately dry air, but when in powder are completely soluble in the strongest alcohol.

Iodine is freely soluble in water which contains iodide of potassium, a brown solution resulting, which has been thought to arise from potassium uniting with two or more equivalents of iodine. No solid compound of the kind, however, has been obtained.

Its eq. is 165·45; symb. $K + I$, or KI.

Bromide of Potassium.—This compound is formed by processes similar to those for preparing the iodide, and is analogous to it in most of its properties. It is very soluble in water, and crystallizes by evaporation in anhydrous cubic crystals, which fuse readily, and decrepitate when heated like sea-salt. It is but slightly soluble in alcohol. Its eq. is 117·55; symb. $K + Br$, or KBr.

Fluoride of Potassium.—This compound is best formed by nearly saturating hydrofluoric acid with carbonate of potassa, evaporating to dryness in platinum, and igniting to expel any excess of acid. The resulting fluoride has a sharp saline taste, is alkaline to test paper, deliquesces in the air, and dissolves freely in water. On evaporating its solution at a temperature of 100° it may be obtained in cubes or rectangular four-sided prisms, which deliquesce rapidly. The solution acts on glass in which it is kept or evaporated. Heated with silicic acid it forms a fusible liquid glass, which when cold is opaque and deliquescent. Water dissolves fluoride of potassium, and the silicic acid is left. Its eq. is 57·83; symb. $K + F$, or KF.

Hydrogen and Potassium.—These substances unite in two proportions, forming in one case a solid, and in the other a gaseous compound. The latter is produced when hydrate of potash is decomposed by iron at a white heat, and it appears also to be generated when potassium burns on the surface of water. It inflames spontaneously in air or oxygen gas; but on standing for some hours over mercury, the greater part, if not the whole of the potassium, is deposited.

The solid hyduret of potassium was made by Gay-Lussac and Thenard, by heating potassium in hydrogen gas. It is a grey, solid substance, which is readily decomposed by heat or contact with water. It does not inflame spontaneously in oxygen gas.

Carburet of Potassium.—This compound has not been obtained in a pure state; but it is thought to form part of the residue in the preparation of potassium from the carbonate by charcoal; for on pouring that matter into water, effervescence ensues owing to the escape of carburetted hydrogen gas, and carbonate of potassa is found in solution.

Sulphurets of Potassium.—Potassium unites readily with sulphur by the aid of gentle heat, emitting so much heat that the mass becomes incandescent. The nature of the product depends on the proportions which are employed. The protosulphuret is readily prepared by decomposing sulphate of potassa by charcoal or hydrogen gas at a red heat. It may be prepared in the moist way by a process which will be mentioned in describing the sulphur-salts.

The protosulphuret of potassium fuses below a red heat, and acquires on cooling a crystalline texture. It has a red colour, its taste is at first strongly alkaline and then sulphurous, has an alkaline reaction with test paper, deliquesces on exposure to the air, and is soluble in water and alcohol. Most of the acids decompose it with evolution of hydrosulphuric acid gas, and without any deposite of sulphur. It takes fire when heated before the blowpipe, and quickly acquires a coating of sulphate of potassa, which stops the combustion; but when mixed in fine division with charcoal, it kindles spontaneously, forming a good pyrophorus.

Its eq. is 55·25; symb. $K + S$, or KS.

The *bisulphuret* is formed by exposing to the air a saturated solution in alcohol of hydrosulphate of sulphuret of potassium ($KS + HS$), until a pellicle begins to form upon its surface, and then evaporating to dryness without further exposure. The first change consists in the oxygen of the air uniting with the hydrogen of the hydrosulphuric acid, the sulphur of which unites with potassium. Then the formation of hyposulphurous acid begins; and as the hyposulphite of potassa is insoluble in alcohol, it gives a pellicle on its surface. It may also be obtained from an aqueous solution of the protosulphuret. This compound, when pure, dissolves in water without colour; but exposed to the air, oxygen is rapidly absorbed, and the solution becomes yellow. The change is effected by one-half of the potassium combining with oxygen and yielding its sulphur to the remainder, by which the bisulphuret of potassium and potassa are formed. Thus $2KS$ yield KS_2, and KO. If the solution continues to be exposed, it again becomes colourless, owing to the conversion of the bisulphuret into hyposulphite of potassa.

Its eq. is 71·35 ; symb. $K + 2S$, or KS_2.

The *tersulphuret* is prepared pure by transmitting the vapour of bisulphuret of carbon over carbonate of potassa at a red heat, as long as carbonic acid or carbonic oxide gases are disengaged. It is also formed when carbonate of potassa is heated to low redness with half its weight of sulphur, until the mass appears in tranquil fusion : the oxygen of 3-4ths of the potassa unites with sulphur to form sulphuric acid, which exactly suffices to neutralize 1-4th of the alkali, and all the carbonic acid is evolved as gas.—Thus

4 eq. Potassa and	10 eq. Sulphur	yield	3 eq. Tersulphuret and	1 eq. Sulphate.
$4KO$	S_{10}		$3KS_3$	KO, SO_3.

This is known under the name of *liver of sulphur.*

Its eq. is 87·45 ; symb. $K + 3S$, or KS_3.

The *quadrosulphuret* is prepared by transmitting the vapour of bisulphuret of carbon over sulphate of potassa at a red heat until carbonic acid gas ceases to be disengaged ; or by conducting the same process with the impure tersulphuret prepared by the second method, until its sulphuric acid and potassa are decomposed.

Its eq. is 103·55 ; symb. $K + 4S$, or KS^4.

The *quintosulphuret* is formed by fusing carbonate of potassa with its own weight of sulphur, the residue containing sulphate of potassa as in preparing the tersulphuret. Each equivalent of potassium unites with five of sulphur, being the highest degree of sulphuration which can be formed by fusion.

Its eq. is 119·65 ; symb. $K + 5S$, or KS_5.

These four last sulphurets are deliquescent in the air, have a sulphureous odour, and are soluble in water ; and those who consider them to decompose water in dissolving, suppose the formation of corresponding compounds of hydrogen and sulphur. On decomposing the solutions with hydrochloric or sulphuric acid, the changes ensue which have already been explained (page 330). As the solution of the quintosulphuret dissolves sulphur, a still higher degree of sulphuration most probably exists.

Two other compounds of sulphur and potassium, the composition of which are K_2S_7, and K_2S_9, have been described. The first of these is produced when sulphate of potassa is heated in a stream of sulphuretted hydrogen ; and the latter, when the quadrosulphuret of potassium is heated in a similar manner. The definite nature of these compounds may be considered doubtful.

Phosphurets of Potassium.—When potassium is heated in phosphuretted hydrogen gas, it takes fire, phosphuret of potassium is formed, and hydrogen set free; and combination is also effected by gently heating phosphorus with potassium. The number and proportion of these compounds have not yet been determined. They decompose water with formation of phosphuretted hydrogen, potassa, and some acid of phosphorus.

Seleniurets of Potassium.—These elements unite when fused together, sometimes with explosive violence, forming a crystalline fusible compound of an iron-grey colour and metallic lustre. It dissolves completely in water, yielding a deep red solution, very similar in taste and odour to solutions of sulphuret of potassium. On adding an acid, hydroselenic acid gas is evolved, and selenium deposited. Solution of potassa dissolves selenium, and gives rise to a seleniuret of potassium and selenite of potassa: and the same compounds are formed when selenium is heated with carbonate of potassa.

SECTION II.

SODIUM.

Hist. and Prep.—The *Natrium* of the Germans; was discovered in 1807, a few days after the discovery of potassium. The first portions of it were obtained by means of galvanism; but it may be procured in much larger quantity by chemical processes, precisely similar to those described in the last section. As sodium may be obtained in much larger quantity than potassium, owing to the fact that it does not combine, like the former, with carbonic oxide, the method of preparing sodium as described by Schœdler (Liebig's Annalen, vol. xx. p. 2) is here briefly noticed. Three pounds of commercial acetate of soda are ignited, and the residue, which weighs 1 lb., consisting of carbonate mixed with charcoal, is further mixed with ¼ lb. of finely-powdered charcoal and ½ lb. of charcoal in coarser particles, to prevent fusion of the mass. It is then heated in the usual manner in an iron bottle, such as is used for holding mercury in commerce. This process is so productive, that in one operation with the above quantities Schœdler obtained 4½ oz. of pure sodium. As a quantity half larger may be heated in such a bottle, it is possible to obtain in one operation upwards of 6 oz. of sodium; and this from the cheapest materials. Sodium thus prepared has been sold at three or four shillings per ounce. It might be made much cheaper even than this, and as it oxidizes less rapidly than potassium, it is much better adapted for experiments of research.

Prop.—It has a strong metallic lustre, and in colour is very analogous to silver. It is so soft at common temperatures, that it may be formed into leaves by the pressure of the fingers. It fuses at 200°, and rises in vapour at a red heat. Its sp. gr. is 0·972. It soon tarnishes on exposure to the air, though less rapidly than potassium. Like that metal, it is instantly oxidized by water, hydrogen gas in temporary union with a little sodium being disengaged. When thrown on cold water, it swims on its surface, and is rapidly oxidized, though in general without inflaming; but with hot water it scintillates, or even takes fire. Ducatel finds that the heat rises high enough for inflammation with cold water, if the sodium be confined to one spot, and the water rest on a non-conducting substance, such as charcoal. (Silliman's Journal, xxv. 90.) In each case soda is generated, and the water acquires an alkaline reaction.

The composition of soda was determined by the same methods as that of potassa, and agreeably to the observations of Berzelius 23·3 may be taken as the eq. of sodium. Its symb. is Na. The composition of the compounds of sodium described in this section is as follows:—

	Sodium.			Equiv.	Formulæ.
Protoxide	. 23·3	1 eq.+Oxygen	8	1 eq.= 31·3	$Na+O$ or NaO.
Peroxide	. 46·6	2 eq.+Do.	24	3 eq.= 70·6	$2Na+3O$ or Na_2O_3.
Chloride	. 23·3	1 eq.+Chlorine	35·42	1 eq.= 58·72	$Na+Cl$ or $NaCl$.
Iodide .	. 23·3	1 eq.+Iodine	126·3	1 eq.=149·6	$Na+I$ or NaI.
Bromide	. 23·3	1 eq.+Bromine	78·4	1 eq.=101·7	$Na+Br$ or $NaBr$.
Fluoride	. 23·3	1 eq.+Fluorine	18·68	1 eq.= 41·98	$Na+F$ or NaF.
Sulphuret	. 23·3	1 eq.+Sulphur	16·1	1 eq.= 39·4	$Na+S$ or NaS.

Soda.—*Prep.*—The protoxide of sodium, commonly called *soda*, and by the Germans *natron*, is formed by the oxidation of sodium in air or water, as potassa is from potassium. In its anhydrous state it is a grey solid, difficult of fusion, and very similar in all its characters to potassa. With water it forms a solid hydrate, easily fusible by heat, which is very caustic, soluble in water and alcohol, has powerful alkaline properties, and in all its chemical relations is exceedingly analogous to potassa. It is prepared from the solution of pure soda, exactly in the same manner as the corresponding preparations of potassa. The solid hydrate is composed of 31·3 parts or 1 eq. of soda, and 9 parts or 1 eq. of water.

Prop.—Soda is readily distinguished from other alkaline bases by the following characters:—1. It yields, with sulphuric acid, a salt which, by its taste and form, is easily recognized as Glauber's salt, or sulphate of soda. 2. Nearly all its salts are soluble in water, and are not precipitated by any reagent. Hydrofluosilicic acid causes, in solutions of soda, a gelatinous precipitate, very similar to that formed in solutions of potash. The antimoniate of potash has lately been proposed as a means of distinguishing soda from potash. A solution of that salt causes, in solutions of soda, a white insoluble precipitate, which is antimoniate of soda. 3. On exposing its salts by means of platinum wire to the blowpipe flame, they communicate to it a rich yellow colour.

Its eq. is 31·3; symb. $\mathrm{Na} + \mathrm{O}$, $\dot{\mathrm{N}}\mathrm{a}$, or NaO.

Peroxide of Sodium.—This compound is formed when sodium is heated to redness in an excess of oxygen gas. It has an orange colour, has neither acid nor alkaline properties, and is resolved by water into soda and oxygen.

Its eq. is 70·6; symb. $2\mathrm{Na} + 3\mathrm{O}$, $\overset{\cdots}{\underline{\mathrm{N}}}\mathrm{a}$, or $\mathrm{Na_2O_3}$.

Chloride of Sodium.—Hist. and Prep.—This compound may be formed directly by burning sodium in chlorine, by heating sodium in hydrochloric acid gas, and by neutralizing soda with hydrochloric acid. It exists as a mineral under the name of *rock salt*, is the chief ingredient of sea-water, and is contained in many saline springs. From these sources are derived the different varieties of common salt, such as rock, bay, fishery, and stoved salt, which differ from each other only in degrees of purity and mode of preparation. The rock and bay salt are the purest, but always contain small quantities of sulphate of magnesia and lime, and chloride of magnesium. These earths may be precipitated as carbonates by boiling a solution of salt for a few minutes with a slight excess of carbonate of soda, filtering the liquid, and neutralizing with hydrochloric acid. On evaporating this solution rapidly, chloride of sodium crystallizes in hollow four-sided pyramids; but it occurs in regular cubic crystals when the solution is allowed to evaporate spontaneously. These crystals contain no water of crystallization, but decrepitate remarkably when heated, owing to the expansion of water mechanically confined within them.

Prop.—Pure chloride of sodium has an agreeably saline taste. It fuses at a red heat, and becomes a transparent brittle mass on cooling. It deliquesces slightly in a moist atmosphere, but undergoes no change when the air is dry. In pure alcohol it is insoluble. It requires twice and a half its weight of water at 60° for solution, and its solubility is not increased by heat. Hydrous sulphuric acid decomposes it with evolution of hydrochloric acid gas, and formation of sulphate of soda.

The uses of chloride of sodium are well known. Besides its employment in seasoning food, and in preserving meat from putrefaction, a property which, when pure, it possesses in a high degree, it is used for various purposes in the arts, especially in the formation of hydrochloric acid and bleaching powder, and in the manufacture of carbonate of soda.

Its eq. is 58·72 ; symb. $Na + Cl$, or $NaCl$.

Iodide of Sodium.—It is obtained pure by processes similar to those for preparing iodide of potassium ; but it is contained in sea-water, in many salt-springs, and in the residual liquor from kelp. It is a neutral compound, deliquescent in the air, soluble in water and alcohol, fuses readily by heat, and is volatile, though in a less degree than iodide of potassium. Evaporated at 123° it crystallizes from its aqueous solution in cubes, which Berzelius found to contain 20·23 per cent. of water.

Its eq. is 149·6 ; symb. $Na + I$, or NaI.

Bromide of Sodium.—This compound is very analogous to sea-salt, and is associated with it in sea-water and most salt-springs. At 86° it crystallizes from its aqueous solution in anhydrous cubes; but at lower temperatures it separates in hexagonal tables, which Mitscherlich found to contain 26·37 per cent. of water, or 4 eq. to 1 eq. of the bromide.

Its eq. is 101·7; symb. $Na + Br$, or $NaBr$.

Fluoride of Sodium.—This compound is formed by neutralizing hydrofluoric acid by soda, and by igniting the double fluoride of sodium and silicon, when the fluoride of silicon is expelled. When obtained by the second process, it crystallizes from its aqueous solution in rhomboidal crystals, but is obtained in cubes, its proper form, by a second crystallization : when carbonate of soda is present, it crystallizes in octohedrons.

Fluoride of sodium in crystals is anhydrous, is almost insoluble in alcohol, and requires 25 times its weight both of hot and cold water for solution. It attacks glass vessels when evaporated in them, and by fusion unites with silicic acid, forming a glass which is more fusible than the pure fluoride; but water dissolves out the fluoride, and leaves the silicic acid.

Its eq. is 41·98; symb. $Na + F$, or NaF.

Sulphuret of Sodium.—The protosulphuret is obtained by processes similar to those for protosulphuret of potassium, to which in its taste and chemical relations it is very similar. A concentrated solution of it yields hydrated, square, four-sided prisms, which, when heated, fuse in their water of crystallization, and then leave a white anhydrous mass. It deliquesces in the air, is very soluble in water, and is also dissolved, though in a smaller degree, by alcohol. In solution it absorbs oxygen very rapidly from the air, and passes into hyposulphite of soda.

Its eq. is 39·4; symb. $Na + S$, or NaS.

Sodium unites with sulphur in other proportions; but the resulting compounds have not been studied.

According to Gmelin of Tübingen, sulphuret of sodium is the colouring principle of *lapis lazuli*, to which the colour of ultramarine is owing; and he has succeeded in preparing artificial ultramarine by heating sulphuret of sodium with a mixture of silicic acid and alumina. (An. de Ch. et Ph. xxxvii. 409.) Artificial ultramarine, thus prepared, is sold in Paris at a moderate price. The finer specimens are quite equal to the native ultramarine, and much less expensive.

SECTION III.

LITHIUM.

Davy succeeded by means of galvanism in obtaining from lithia a white-coloured metal like sodium; but it was oxidized, and thus reconverted into lithia, with such rapidity, that its properties could not be farther examined. Its eq., inferred from the composition of sulphate of lithia by Stromeyer and Thomson, is 10; but the accuracy of this estimate is rendered doubtful by the experiments of M. Herrman, according to which 6 is a nearer estimate. Its symb. is L. The compounds of lithium described in this section are thus constituted:—

	Lithium.			Equiv.	Formulæ.
Lithia .	6	1 eq.+Oxygen .	8	1 eq.=14	$L+O$ or LO.
Chloride .	6	1 eq.+Chlorine .	35·42	1 eq.=41·42	$L+Cl$ or LCl.
Fluoride .	6	1 eq.+Fluorine .	18·68	1 eq.=24·68	$L+F$ or LF.

Lithia.—Hist.—This, the only known oxide of lithium, was discovered in 1818 by M. Arfwedson (An. de Ch. et Ph. x.) in a mineral called *petalite;* and its presence has since been detected in spodumene, lepidolite, and in several varieties of mica. Berzelius has found it also in the waters of Carlsbad in Bohemia. From the circumstance of its having been first obtained from an earthy mineral, Arfwedson gave it the name of *lithion*, (from λιθειος, *lapideus*,) a term since changed in this country to *lithia.* It has hitherto been procured in small quantity only, because spodumene and petalite are rare, and do not contain more than 6 or 8 per cent. of the alkali. It is combined in these two minerals with silicic acid and alumina, whereas potassa is likewise present in lepidolite and lithion-mica, and therefore lithia should be prepared solely from the former.

Prep.—The best process for preparing lithia is that which was suggested by Berzelius. One part of petalite or spodumene, in fine powder, is mixed intimately with two parts of fluor-spar, and the mixture is heated with three or four times its weight of sulphuric acid, as long as any acid vapours are disengaged. The silicic acid of the mineral is attacked by hydrofluoric acid, and dissipated in the form of fluosilicic acid gas, while the alumina and lithia unite with sulphuric acid. After dissolving these salts in water, the solution is boiled with pure ammonia to precipitate the alumina: it is then filtered and evaporated to dryness, and the dry mass heated to redness to expel the sulphate of ammonia. The residue is pure sulphate of lithia.

Prop.—Lithia, in its alkalinity, in forming a hydrate with water, and in its chemical relations, is closely allied to potassa and soda. It is distinguished from them by its greater neutralizing power, by forming sparingly soluble compounds with carbonic and phosphoric acids, and by its salts, when heated on platinum wire before the blowpipe, tinging the flame of a crimson colour. Also, when fused on platinum foil, it attacks that metal and leaves a dull yellow trace round the spot where it lay. It is distinguished from baryta, strontia, and lime, by forming soluble salts with sulphuric and oxalic acids, and from magnesia by its carbonate, though sparingly soluble in water, forming with it a solution which has an alkaline reaction. Its eq. is 14; symb. $L + O$, $\dot{L}$, or LO.

Chloride of Lithium.—It is readily obtained by dissolving lithia or its carbonate in hydrochloric acid. Like the chlorides of sodium and potassium, it yields by evaporation in a warm place colourless, anhydrous, cubic crystals, which differ from those chlorides in being very deliquescent, dissolving freely in alcohol as well as water, and in its alcoholic solution burning with a red flame.

Its eq. is 41·42; symb. $L + Cl$, or LCl.

The iodide and bromide of lithium have not been examined.

Fluoride of Lithium.—This is a fusible compound, prepared by dissolving lithia in hydrofluoric acid, and possesses about the same solubility in water as the carbonate.

ORDER II.

METALLIC BASES OF THE ALKALINE EARTHS.

SECTION IV.

BARIUM.

Hist. and Prep.—Davy discovered *barium*, the metallic base of baryta, in the year 1808, by a process suggested by Berzelius and Pontin. It consists in forming carbonate of baryta into a paste with water, placing a globule of mercury in a little hollow made in its surface, and laying the paste on a platinum tray which communicated with the positive pole of a galvanic battery of 100 double plates, while the negative wire was in contact with the mercury. The baryta was decomposed, and its barium combined with mercury. This amalgam was then heated in a vessel free from air, by which means the mercury was expelled, and barium obtained in a pure form.

Prop.—A dark grey-coloured metal, with a lustre inferior to cast iron. It is far denser than water, for it sinks rapidly in strong sulphuric acid. It attracts oxygen with avidity from the air, and in doing so yields a white powder, which is baryta. It effervesces strongly from the escape of hydrogen gas when thrown into water, and a solution of baryta is produced. It has hitherto been obtained in very minute quantities, and consequently its properties have not been determined with precision.

The eq .of barium, deduced from the analyses of the chloride made by Berzelius and myself, is 68·7. Its symb. is Ba. The composition of its compounds described in this section is as follows:—

	Barium.			Equiv.	Formulæ.
Protoxide .	68·7	1 eq.+Oxygen	8	1 eq.= 76·7	$Ba+O$ or BaO.
Peroxide .	68·7	1 eq.+Ditto	16	2 eq.= 84·7	$Ba+2O$ or BaO_2.
Chloride .	68·7	1 eq.+Chlorine	35·42	1 eq.=104·12	$Ba+Cl$ or $BaCl$.
Iodide .	68·7	1 eq.+Iodine	126·3	1 eq.=195·0	$Ba+I$ or BaI.
Bromide .	68·7	1 eq.+Bromine	78·4	1 eq.=147·1	$Ba+Br$ or $BaBr$.
Fluoride .	68·7	1 eq.+Fluorine	18·68	1 eq.= 87·38	$Ba+F$ or BaF.
Sulphuret .	68·7	1 eq.+Sulphur	16·1	1 eq.= 84·8	$Ba+S$ or BaS.

Protoxide of Barium.—Hist. and Prep.—Barytes, or *Baryta*, so called from the great density of its compounds, (from βαρυς, heavy,) was discovered in the year 1774 by Scheele. It is the sole product of the oxidation of barium in air or water. It may be prepared by decomposing nitrate of baryta at a red heat; or by exposing carbonate of baryta contained in a black-lead crucible to an intense white heat, a process which succeeds much better when the carbonate is intimately mixed with charcoal.

Prop.—A grey powder, the sp. gr. of which is about 4. It requires a very high temperature for fusion; has a sharp caustic alkaline taste, converts vegetable blue colours to green, and neutralizes the strongest acids. Its alkalinity, therefore, is equally distinct as that of potassa or soda; but it is much less caustic and less soluble in water than those alkalies. In pure alcohol it is insoluble. It has an exceedingly strong affinity for water. When mixed with that liquid it slakes in the same manner as quicklime, but with the evolution of a more intense heat, which, according to Döbereiner, sometimes amounts to incandescence. The result is a white bulky hydrate, fusible at a red heat, and which bears the highest temperature of a smith's forge without parting with its water. It is composed of 76·7 parts or 1 eq. of baryta, and 9 parts or 1 eq. of water.

Hydrate of baryta dissolves in three times its weight of boiling water, and in twenty parts of water at the temperature of 60° F. (Davy.) A saturated solution of baryta in boiling water deposits, in cooling, transparent, flattened prismatic crystals, which are composed, according to Phillips, of 76·7 parts or 1 eq. of baryta, and 90 parts or 10 eq. of water. Smith states, however, that the quantity of water amounts only to 81 parts or 9 eq. He has also pointed out the existence of a hydrate containing only 2 eq. of water; it is a white powder which is formed by exposing the crystallized hydrate to the temperature of a sand-bath. (Phil. Mag. and An. vi. 53, and ix. 87.)

The aqueous solution of baryta is an excellent test of the presence of carbonic acid in the atmosphere or in other gaseous mixtures. The carbonic acid unites with the baryta, and a white insoluble precipitate, carbonate of baryta, subsides.

Baryta is distinguished from all other substances by the following characters:—1. By dissolving in water and forming an alkaline solution. 2. By all its soluble salts being precipitated as white carbonate of baryta by alkaline carbonates, and as sulphate of baryta, which is insoluble both in acid and alkaline solutions, by sulphuric acid or any soluble sulphate. 3. By the characters of chloride of barium, formed by the action of hydrochloric acid on baryta.

The readiest method of preparing the soluble salts of baryta is by dissolving the carbonate in dilute acid. All of its soluble salts are poisonous; and the carbonate, from being dissolved by the juices of the stomach, likewise acts as a poison. The sulphate, from its insolubility, is inert.

Its eq. is 76·7; symb. $Ba + O$, $\dot{Ba}$, or BaO.

Peroxide of Barium.—This oxide, which is used by Thenard in preparing peroxide of hydrogen, may be formed by conducting dry oxygen gas over pure baryta at a low red heat. A still easier process, given by Wöhler and Liebig, is to heat pure baryta to low redness in a platinum crucible, and then gradually to add chlorate of potassa in the ratio of about one part of the latter to four of the former. The oxygen of the chlorate goes over to the baryta, and chloride of potassium is generated. Cold water afterwards removes the chloride, and the peroxide of barium is left as a white hydrate with 6 eq. of water, its formula being $BaO_2 + 6$ aq.

Chloride of Barium.—It is generated when chlorine gas is conducted over baryta at a red heat, oxygen gas being disengaged; but it is most conveniently prepared by dissolving carbonate of baryta in hydrochloric acid diluted with about three times its weight of water, or by decomposing a solution of sulphuret of barium with hydrochloric acid. On concentrating its solution, the chloride crystallizes on cooling in flat four-sided tables bevelled at the edges, very like crystals of heavy spar. These crystals consist of 104·12 parts or 1 eq. of chloride of barium, and 18 parts or 2 eq. of water; its formula being $BaCl + 2$ aq. They do not change in ordinary states of the air; but in a very dry atmosphere at 60° they lose all their water; and recover it again in a moist air. They are still more rapidly rendered anhydrous at 212°, and fusion ensues at a full red heat. They are insoluble in strong alcohol: 100 parts of water dissolve 43·5 at 60° and 78 at 222°, which is the boiling point of the solution. Its eq. is 104·12; symb. $Ba + Cl$, or $BaCl$.

Iodide of Barium.—This compound may be formed in the same way as iodide of potassium. It is very soluble in water, and crystallizes in small colourless needles, which deliquesce slightly. On exposure to the air a portion of carbonate of baryta is formed, and iodine set free, which probably forms a periodide of barium.

Its eq. is 159; symb. $Ba + I$, or BaI.

Bromide of Barium.—It was prepared by M. Henry, jun., who has examined it, by boiling protobromide of iron with moist carbonate of baryta in excess, evaporating the filtered solution, and heating the residue to redness. The product crystallizes by careful evaporation in white rhombic prisms, which have a bitter taste, are slightly deliquescent, and are soluble in water and alcohol.

Its eq. is 147·1; symb. $Ba + Br$, or $BaBr$.

Fluoride of Barium.—On digesting recently precipitated and moist carbonate of baryta in hydrofluoric acid, carbonic acid is expelled, and fluoride of barium collects in the form of a white powder, which bears a red heat without decomposition. It is sparingly soluble in water, and by evaporation separates in crystalline grains. It is soluble in nitric and hydrochloric acids.

Its eq. is 87·38; symb. Ba + F, or BaF.

Sulphuret of Barium.—Prep.—This compound may be formed by transmitting dry hydrosulphuric acid gas over pure baryta at a red heat; and by the action of hydrogen gas or charcoal on sulphate of baryta. The easiest process is to mix sulphate of baryta in fine powder into a paste with an equal volume of fluor, place it in a hessian crucible on which a cover is luted, and expose it to a white heat for an hour or two, raising the temperature slowly. On pouring hot water on the ignited mass, the sulphuret of barium is dissolved, and may be separated from undecomposed sulphate and excess of charcoal by filtration.

Protosulphuret of barium is very soluble in hot water, and the solution if saturated deposits colourless crystals on cooling, which are sulphuret of barium with water of crystallization. The solution has a sulphurous odour, and absorbs oxygen and carbonic acid from the air, yielding carbonate and hyposulphite of baryta. Boiled with sulphur it yields a yellow solution, and contains a persulphuret of barium.

Sulphuret of barium supplies a ready mode of obtaining pure baryta and its salts, when the carbonate cannot be obtained. Thus its solution boiled with successive portions of black oxide of copper until it ceases to precipitate a salt of lead black, yields pure baryta, which should be filtered while hot to separate the sulphuret of copper: it is apt to retain for a short time, traces of oxide of copper. With a solution of carbonate of potassa, carbonate of baryta falls, and sulphuret of potassium remains in solution; and with hydrochloric acid it interchanges elements, by which hydrosulphuric acid and chloride of barium are formed. The sulphuret of barium is now much used in organic researches, particularly in purifying vegetable acids, such as malic acid. (Liebig.) Its eq. is 84·8; symb. Ba + S, or BaS.

SECTION V.

STRONTIUM.

Davy discovered the metallic base of strontia, called *strontium*, by a process analogous to that described in the last section. All that is known respecting its properties is, that it is a heavy metal, similar in appearance to barium, that it decomposes water with evolution of hydrogen gas, and oxidizes quickly in the air, being converted in both cases into strontia, which is the protoxide of the metal.

The eq. of strontium, deduced from the experiments of Stromeyer, is 43·8; its symb. Sr. The composition of its several compounds described in this section is as follows:—

	Strontium.			Equiv.	Formulæ.
Protoxide . .	43·8	1 eq.+Oxygen	8	1 eq.= 51·8	Sr+O or SO.
Peroxide . .	43·8	1 eq.+Do.	16	2 eq.= 59·8	Sr+2O or SO_2.
Chloride . .	43·8	1 eq.+Chlorine	35·42	1 eq.= 79·22	Sr+Cl or SrCl.
Iodide . .	43·8	1 eq.+Iodine	126·3	1 eq.=170·1	Sr+I or SrI.
Fluoride . .	43·8	1 eq.+Fluorine	18·68	1 eq.= 62·48	Sr+F or Srf.
Sulphuret . .	43·8	1 eq.+Sulphur	16·1	1 eq.= 59·9	Sr+S or SrS.

Protoxide of Strontium.—Hist.—From the close resemblance between baryta and strontia, these substances were once supposed to be identical. Crawford, however, and Sulzer noticed a difference between them; but the existence of strontia was first established with certainty in the year 1792 by Hope,[*] and the discovery was made about the same time by Klaproth.[†] It was originally extracted from strontianite, native carbonate of strontia, a mineral found at Strontian, in Scotland; and hence the origin of the term *Strontites,* or *Strontia,* by which the earth itself is designated.

Prep. and Prop.—Pure strontia may be prepared from nitrate and carbonate of strontia, in the same manner as baryta. It resembles this earth in appearance, in infusibility, and in possessing distinct alkaline properties. It slakes when mixed with water, causing intense heat, and forming a white solid hydrate, which consists of 51·8 parts or 1 eq. of strontia, and 9 parts or 1 eq. of water. Hydrate of strontia fuses readily at a red heat. It is insoluble in alcohol. Boiling water dissolves it freely, and a hot saturated solution, on cooling, deposits transparent crystals in the form of thin quadrangular tables, which consist of 1 eq. of strontia and 10 eq. of water according to Phillips. Smith states its composition to be $SrO + 9HO$. He also states that dried at 212° it becomes $SrO + HO$, and becomes anhydrous on exposure to a red heat. It requires 50 times its weight of water at 60° for solution, and twice its weight at 212° F. (Dalton.)

The solution of strontia has a caustic taste and alkaline reaction. Like the solution of baryta, it is a delicate test of the presence of carbonic acid in air or other gaseous mixtures, forming with it the insoluble carbonate of strontia.

The salts of strontia are best prepared from the native carbonate. Like those of baryta, they are precipitated by alkaline carbonates, and by sulphuric acid or soluble sulphates. But sulphate of strontia is less insoluble than sulphate of baryta: on adding sulphate of soda in excess to a barytic solution, baryta cannot afterwards be found in the liquid by any precipitant; but when a solution of strontia is thus treated, so much sulphate of strontia remains in solution, that the filtered liquid yields a white precipitate with carbonate of soda. The salts of strontia are not poisonous; and most of them, when heated on platinum wire before the blowpipe, communicate to the flame a red tint.

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[*] Edin. Philos. Trans., iv. 3.

[†] Klaproth's Contributions, i.

Its eq. is 51·8; symb. $Sr + O$, $\dot{Sr}$, or SrO.

Peroxide of Strontium is prepared in the same way as peroxide of barium, and like it, is resolved by dilute acids into strontia and oxygen, the latter of which forms peroxide of hydrogen with the water.

Chloride of Strontium.—This compound is formed by processes similar to those for preparing chloride of barium, and crystallizes from its solution in colourless prismatic crystals, which deliquesce in a moist atmosphere, require only twice their weight of water at 60° for solution, and still less of boiling water, and are soluble in alcohol. The alcoholic solution, when set on fire, burns with a red flame. These characters afford a certain mode of distinguishing strontia from baryta. The crystals consist of 79·22 parts or 1 eq. of chloride of strontium, and 81 parts or 9 eq. of water, which are expelled by heat. The anhydrous chloride fuses at a red heat, and yields a white crystalline brittle mass on cooling.

Its eq. is 79·22; symb. $Sr + Cl$, or $SrCl$.

Iodide of Strontium may be prepared in the same manner as that of barium. It is very soluble in water, and fuses without decomposition in close vessels; but when heated to redness in the open air, iodine escapes, and strontia is generated.

Fluoride of Strontium is obtained in the same way as fluoride of barium, and is a white powder of sparing solubility.

Protosulphuret of Strontium is similar in its properties and mode of preparation to sulphuret of barium, and may be applied to similar uses. Strontium also combines with more than one equivalent of sulphur; but these compounds have not been examined.

SECTION VI.

CALCIUM.

The existence of calcium, the metallic base of lime, was demonstrated by Davy by a process similar to that described in the section on barium. It is of a whiter colour than barium or strontium, and is converted into lime by being oxidized. Its other properties are unknown.

According to the analysis of chloride of calcium by Berzelius, the eq. of calcium is 20·5; its symb. is Ca. Its compounds described in this section are composed as follows:—

	Calcium.			Equiv.	Formulæ.
Protoxide .	20·5	1 eq.+Oxygen	8	1 eq.= 28·5	Ca+O or CaO.
Peroxide .	20·5	1 eq.+ . .	16·0	2 eq.= 36·5	Ca+2O or CaO_2.
Chloride .	20·5	1 eq.+Chlorine	35·42	1 eq.= 55·92	Ca+Cl or CaCl.
Iodide .	20·5	1 eq.+Iodine	126·3	1 eq.=146·8	Ca+I or CaI.
Bromide .	20·5	1 eq.+Bromine	78·4	1 eq.= 98·9	Ca+Br or CaBr.
Fluoride .	20·5	1 eq.+Fluorine	18·68	1 eq.= 39·18	Ca+F or CaF.
Sulphuret .	20·5	1 eq.+Sulphur	16·1	1 eq.= 36·6	Ca+S or CaS.
Bisulphuret .	20·5	1 eq.+ . .	32·2	2 eq.= 52·7	Ca+2S or CaS_2.
Quintosulphuret	20·5	1 eq.+ . .	80·5	5 eq.=101	Ca+5S or CaS_5.
Phosphuret .	20·5	1 eq.+Phosph.	15·7	1 eq.= 36·2	Ca+P or CaP.

Protoxide of Calcium.—*Prep.*—This compound, commonly known by the name of *lime* and *quicklime*, is obtained by exposing carbonate of lime to a strong red heat, so as to expel its carbonic acid. If lime of great purity is required, it should be prepared from pure carbonate of lime, such as Iceland spar or Carrara marble; but in burning lime in lime-kilns for making mortar, common limestone is employed. The expulsion of carbonic acid is facilitated by mixing the carbonate with combustible substances, in which case carbonic oxide is generated. A current of air also greatly facilitates the burning of lime; for in close vessels it is hardly possible to expel the whole carbonic acid. The effect of a current of air is partly due to the diffusion of one gas in another.

Prop.—It is a brittle white earthy solid, the sp. gr. of which is about 2·3. It phosphoresces powerfully when heated to full redness, a property which it possesses in common with strontia and baryta. It is one of the most infusible bodies known, fusing with difficulty even by the heat of the oxy-hydrogen blowpipe. It has a powerful affinity for water, and the combination is attended with great increase of temperature, and formation of a white bulky hydrate, which is composed of 28·5 parts or 1 eq. of lime, and 9 parts or 1 eq. of water. The process of *slaking* lime consists in forming this hydrate, and the hydrate itself is called *slaked* lime. It differs from the hydrate of baryta in parting with its water at a red heat.

Hydrate of lime is dissolved very sparingly by water, and it is a singular fact, first noticed, I believe, by Dalton, that it is more soluble in cold than in hot water. Thus he found that one grain of lime requires for solution

778 grains of water	at 60° F.
972	130°
1270	212°

And, consequently, on heating a solution of *lime water*, which has been prepared in the cold, deposition of lime ensues. This fact was determined experimentally by Phillips, who has likewise observed that water at 32° is capable of dissolving twice as much lime as at 212° F. Owing to this circumstance pure lime cannot be made to crystallize in the same manner as baryta or strontia; but Gay-Lussac succeeded in obtaining crystals of lime by evaporating lime water under the exhausted receiver of an air-pump by means of sulphuric acid. Small transparent crystals, in the form of regular hexahedrons, were deposited, which consist of water and lime in the same proportion as in the hydrate above mentioned.

Lime water is prepared by mixing hydrate of lime with water, agitating the mixture repeatedly, and then setting it aside in a well-stopped bottle until the undissolved parts shall have subsided. The substance called *milk* or *cream* of lime is made by mixing hydrate of lime with a sufficient quantity of water to give it the liquid form; —it is merely lime water in which hydrate of lime is mechanically suspended.

Lime water has a harsh acrid taste, and converts vegetable blue colours to green.—It agrees, therefore, with baryta and strontia in possessing distinct alkaline properties. Like the solution of these earths, it has a strong affinity for carbonic acid, and forms with it an insoluble carbonate. On this account lime water should be carefully protected from the air. For the same reason, lime water is rendered turbid by a solution of carbonic acid; but on adding a large quantity of the acid, the transparency of the solution is completely restored, because carbonate of lime is soluble in an excess of carbonic acid. The action of this acid on the solutions of baryta and strontia is precisely similar.

The salts of lime, which are easily prepared by the action of acids on pure marble, are in many respects similarly affected by reagents, as those of baryta and strontia. They are precipitated, for example, by alkaline carbonates. Sulphuric acid and soluble sulphates likewise precipitate lime from a moderately strong solution. But sulphate of lime has a considerable degree of solubility. Thus, a dilute solution of a salt of lime is not precipitated at all by sulphuric acid; and when the sulphate of lime is deposited, it may be redissolved by the addition of nitric acid.

The most delicate test of the presence of lime is oxalate of ammonia or potassa; for of all the salts of lime, the oxalate is the most insoluble in water. This serves to distinguish lime from most substances, though not from baryta and strontia; because the oxalates of baryta and strontia, especially the latter, are likewise sparingly soluble.—All these oxalates dissolve readily in water acidulated with nitric or hydrochloric acid. It is distinguished from baryta and strontia by the fact, that nitrate of lime yields prismatic crystals by evaporation, is deliquescent in a high degree, and very soluble in alcohol; while the nitrates of baryta and strontia crystallize in regular octohedrons, or segments of the octohedron, undergo no change on exposure to the air, except when it is very moist, and do not dissolve in pure alcohol.

The salts of lime, when heated before the blowpipe, or when their solutions in alcohol are set on fire, communicate to the flame a dull brownish-red colour.

Its eq. is 28·5; symb. $\mathrm{Ca} + \mathrm{O}$, $\dot{\mathrm{Ca}}$, or CaO.

Peroxide of Calcium.—This oxide is prepared in the same way as peroxide of barium, and is similar to it in its properties.

Chloride of Calcium.—This compound exists in sea-water and in many saline springs, is the residue of the process for preparing ammonia, and is readily formed by dissolving marble or chalk in hydrochloric acid. On evaporating its solution to the consistence of a syrup, the chloride crystallizes on cooling in irregular, colourless, prismatic crystals, which consist of 55·92 parts or 1 eq. of chloride of calcium, and 54 parts or 6 eq. of water. By heat it loses its water, and at a gentle red heat fuses; but on exposure to the air it rapidly recovers its water of crystallization and then deliquesces. Owing to its strong affinity for water, it is much used for frigorific mixtures with snow; but for this purpose the hydrous chloride is preferable, as prepared by evaporating its solution so far, that the whole becomes a solid mass on removal from the fire, reducing it when cold quickly to powder, and preserving it in bottles closed with great care. It is also used for drying gases, and ethereal and oily liquids, and, in organic analysis, to absorb the water formed, and thus determine the amount of hydrogen. Chloride of calcium is very soluble in alcohol, and forms with it a definite compound.

Its eq. is 55·92; symb. $\mathrm{Ca} + \mathrm{Cl}$, or CaCl.

Iodide of Calcium.—This compound may be prepared by digesting hydrate of lime with protiodide of iron. It is deliquescent and very soluble in water, sustains a red heat unchanged in close vessels, but when heated in the open air its iodine is replaced by oxygen, and lime remains. The solution of iodide of calcium dissolves a large quantity of iodine, and on evaporating the brown solution in vacuo above a vessel with dry carbonate of potassa, a periodide of calcium crystallizes in large black prisms of a metallic lustre.

Its eq. is 46·8; symb. $\mathrm{Ca} + \mathrm{I}$, or CaI.

Bromide of Calcium.—It was prepared by Henry by digesting hydrate of lime with a solution of protobromide of iron, and crystallizes in acicular crystals, which are very deliquescent, and extremely soluble in alcohol and water. It is very analogous in taste and properties to chloride of calcium, fuses by heat, but in open vessels suffers partial decomposition.

Its eq. is 98·9; symb. $Ca + Br$, or $CaBr$.

Fluoride of Calcium.—Hist. and Prep.—This is a natural product, which frequently accompanies metallic ores, especially those of lead and tin, often occurs in cubic crystals, and is well known under the name of *fluor* or *Derbyshire spar.* The crystals found in the lead mines of Derbyshire are remarkable for the largeness of their size, the regularity of their form, and the variety and beauty of their colours. It may be prepared artificially by digesting moist, recently precipitated carbonate of lime in an excess of hydrofluoric acid; or by mixing a solution of chloride of calcium with fluoride of potassium or sodium. As prepared in the latter mode, it is a bulky gelatinous mass, which it is very difficult to wash; whereas the former method gives it in the state of a granular white powder, which may be washed with ease.

Prop.—Fluoride of calcium fuses at a red heat without farther change. It is nearly insoluble in water, slightly soluble in hot diluted hydrochloric acid, and is decomposed by sulphuric acid aided by gentle heat. It is in a small degree decomposed by boiling nitric acid. Fused with carbonate of potassa, carbonate of lime and fluoride of potassium are generated.

Fluor-spar is much used in forming vases, as a flux in metallurgic processes, and in the preparation of hydrofluoric acid.

It is very remarkable that fluoride of calcium is invariably present in the bones of animals. It was first observed in the enamel of the teeth, which probably contains a large proportion, and may owe its hardness to this circumstance. It has been found in every specimen of fossil bones or coprolites in which it has been looked for, and it was at one time believed that it occurred in much larger quantity in fossil than in recent bones. Some specimens of fossil bones are said to have yielded 10 or 12 per cent., or even more. But Daubeny has shewn that its proportion is very variable, and that it is more difficult to detect it and to determine its amount in recent than in fossil bones, from the presence of organic matter. There can be no doubt that it serves a useful purpose in the bones; but while it was believed to be quite insoluble, it was difficult to account for its introduction into the system. The recent experiments of Dr. Wilson have shewn not only that fluoride of calcium is soluble in water, though sparingly so, but that it is very universally diffused in all natural waters, including sea-water. It is possible that fossil bones, if they really contain more of the fluoride than recent bones, may have derived a part of it from water which has percolated through them; but it may be regarded as certain that fluoride of calcium is never absent from recent bones, nor indeed from the flesh and food of animals. It is very probable, also, that it is an essential constituent of the ashes of vegetables, and that the plants derive it, through the agency of water, from the soil. As an essential constituent of organized beings, it acquires a great additional importance. Daubeny conjectures that its presence in the bones may have the effect of preventing any approach to a crystalline structure in the phosphate of lime, and thus giving to the bones the toughness which is so essential to them.

Its eq. is 39·18; symb. $Ca + F$, or CaF.

Protosulphuret of Calcium.—*Prep.*—By reduction from the sulphate by hydrogen or charcoal, and when pure is white with a reddish tint, and is very sparingly soluble in water. It has the property, in common with sulphuret of barium, of being phosphorescent after exposure to light, and appears to be the essential ingredient of Canton's phosphorus.

When 3 parts of slaked lime, 1 of sulphur, and 20 of water are boiled together for an hour, and the solution, without separation from the sediment, is set aside in a corked flask for a few days, a copious deposite is formed of orange-coloured crystals, which, when slowly formed, are flat quadrilateral prisms. These, from the analysis of Herschel, appear to be bisulphuret of calcium with 3 eq. of water. They are decomposed by exposure to the air, and are of sparing solubility in water.

When either of the foregoing sulphurets is boiled in water along with sulphur, a yellow solution is formed containing calcium combined with 5 eq. of sulphur.

Phosphuret of Calcium.—It is formed by passing the vapour of phosphorus over fragments of quicklime at a low red heat, when a brown matter is formed consisting of phosphate of lime and phosphuret of calcium. When put into water, mutual decomposition ensues, and phosphuretted hydrogen, hypophosphorous acid, and phosphoric acid are generated.

SECTION VII.

MAGNESIUM.

Hist. and Prep.—The galvanic researches of Davy demonstrated the existence of magnesium, though he obtained it in a quantity too minute for determining its properties. It was prepared by Bussy, in the year 1830, by the action of potassium on chloride of magnesium. For this purpose five or six pieces of potassium, of the size of peas, were introduced into a glass tube, the sealed extremity of which was bent in the form of a retort, and upon the potassium were laid fragments of chloride of magnesium. The latter being then heated to near its point of fusion, a lamp was applied to the potassium, and its vapour transmitted through the mass of heated chloride. Vivid incandescence immediately took place, and on putting the mass, after cooling, into water, the chloride of potassium with undecomposed chloride of magnesium was dissolved, and metallic magnesium subsided. These results have been since confirmed by Liebig. (An. de Ch. et Ph. xlvi. 435.)

Prop.—Magnesium has a brilliant metallic lustre, and a white colour like silver, is very malleable, and fuses at a red heat. Moist air oxidizes it superficially; but it undergoes no change in a dry air, and may be boiled in water without oxidation. Heated to redness in air or oxygen gas, it burns with brilliancy, yielding magnesia; and it inflames spontaneously in chlorine gas. It is readily disolved by dilute acids with disengagement of hydrogen, and the solution is found to contain a pure salt of magnesia.

The eq. of magnesium, inferred by Berzelius from the quantity of sulphate obtained from a known weight of pure magnesia, is 12·7; its symb. is Mg. Its compounds described in this section are composed as follows:—

	Magnesium.			Equiv.	Formulæ.
Protoxide .	12·7	1 eq.+Oxygen	8	1 eq.= 20·7	$Mg+O$ or MgO.
Chloride .	12·7	1 eq.+Chlorine	35·42	1 eq.= 48·12	$Mg+Cl$ or $MgCl$.
Iodide .	12·7	1 eq.+Iodine	126·3	1 eq.=139	$Mg+I$ or MgI.
Bromide .	12·7	1 eq.+Bromine	78·4	1 eq.= 91·1	$Mg+Br$ or $MgBr$.
Fluoride .	12·7	1 eq.+Fluorine	18·68	1 eq.= 31·38	$Mg+F$ or MgF.

Protoxide of Magnesium.—*Prep.*—This, the only known oxide of magnesium, commonly known by the name of *magnesia*, is best obtained by exposing carbonate of magnesia to a very strong red heat, by which its carbonic acid is expelled. It is a white friable powder, of an earthy appearance; and when pure it has neither taste nor odour. Its sp. gr. is about 2·3, and it is exceedingly infusible. It has a weaker affinity than lime for water; for though it forms a hydrate when moistened, the combination is effected with hardly any disengagement of heat, and the product is readily decomposed by a red heat. According to the analysis of Stromeyer, the native hydrate contains 1 eq. of each of its constituents; and the results of the analysis of Berzelius and Fyfe accord very nearly with this proportion. It has generally been thought that magnesia formed several hydrates; but the recent observations of Rees indicate that the artificial hydrates have the same composition as the native. (Phil. Mag. and An. x. 454.)

Prop.—Very sparingly soluble in water. According to Fyfe, it requires 5142 times its weight of water at 60°, and 36,000 of boiling water for solution. The resulting liquid does not change the colour of violets; but when pure magnesia is put upon moistened turmeric paper, it causes a brown stain. From this there is no doubt that the inaction of magnesia with respect to vegetable colours, when tried in the ordinary mode, is owing to its insolubility.—It possesses the still more essential character of alkalinity, that, namely, of forming neutral salts with acids, in an eminent degree. It absorbs both water and carbonic acid when exposed to the atmosphere, and therefore should be kept in well-closed phials.

Magnesia is characterized by the following properties:—With nitric and hydrochloric acids it forms salts which are soluble in alcohol, and exceedingly deliquescent. The sulphate of magnesia is very soluble in water, a circumstance by which it is distinguished from the other alkaline earths. Magnesia is precipitated from its salts as a bulky hydrate by the pure alkalies. It is precipitated as carbonate of magnesia, by the carbonates of potassa and soda; but the bicarbonates, and the common carbonate of ammonia, do not precipitate it in the cold. If moderately diluted, the salts of magnesia are not precipitated by oxalate of ammonia. By means of this reagent magnesia may be both distinguished and separated from lime.

Its eq. is 20·7; symb. $\mathrm{Mg} + \mathrm{O}$, $\dot{\mathrm{Mg}}$, or MgO.

Chloride.—This compound may be prepared by transmitting dry chlorine gas over a mixture of magnesia and charcoal at a red heat; but Liebig has given an easier process, which consists in dissolving magnesia in hydrochloric acid, evaporating to dryness, mixing the residue with its own weight of hydrochlorate of ammonia, and projecting the mixture in successive portions into a platinum crucible at a red heat. As soon as the ammoniacal salt is wholly expelled, the fused chloride of magnesium is left in a state of tranquil fusion, and on cooling becomes a transparent colourless mass, which is highly deliquescent, and is very soluble in alcohol and water.

Its eq. is 48·12; symb. MgCl.

Iodide of Magnesium is obtained by dissolving magnesia in hydriodic acid, is very soluble in water, and is only known in solution.

Bromide of Magnesium, obtained by dissolving magnesia in hydrobromic acid, crystallizes in small acicular prisms, which have a sharp taste, are deliquescent, and very soluble in water and alcohol. It is decomposed by a strong heat.

Fluoride of Magnesium is prepared by digesting magnesia in hydrofluoric acid in excess. It is insoluble in water and in excess of hydrofluoric acid, and bears a red heat without decomposition.

ORDER III.

METALLIC BASES OF THE EARTHS.

SECTION VIII.

ALUMINIUM.

Hist.—That alumina is an oxidized body was proved by Davy, who found that potassa is generated when the vapour of potassium is brought into contact with pure alumina heated to whiteness; and it was inferred, chiefly by analogical reasoning, to be a metallic oxide. The propriety of this inference has been demonstrated by Wöhler, who has procured *aluminium*, the metallic base of alumina, in a pure state. (Edinburgh Journal of Science, No. xvii. 178.)

Prep.—Depends on the property which potassium possesses, of decomposing the chloride of aluminium. Decomposition is effected by aid of a moderate increase of temperature; but the action is so violent, and accompanied with such intense heat, that the process cannot be safely conducted in glass vessels. Wöhler succeeded with a platinum crucible, retaining the cover in its place by a piece of wire. The heat developed during the action was so great, that the crucible, though but gently heated externally, suddenly became red-hot. The platinum is scarcely attacked during the process; but to prevent the possibility of error from this source, the decomposition was also effected in a crucible of porcelain. The potassium employed for the purpose should be quite free from carbon, and the quantity operated on at one time not exceed the size of ten peas. The heat was applied by means of a spirit-lamp, and continued until the action was completed. The proportion of the materials requires to be carefully adjusted; for the potassium should be in such quantity as to prevent any chloride of aluminium from subliming during the process, but not so much as to yield an alkaline solution when the product is put into water. The matter contained in the crucible at the close of the operation is in general completely fused, and of a dark grey colour. When *quite cold*, the crucible is put into a large glass full of water, in which the saline matter is dissolved, with slight disengagement of hydrogen of an offensive odour; and a grey powder separates, which on close inspection, especially in sunshine, is found to consist solely of minute scales of metal. These scales, after being well washed in *cold* water, are pure aluminium. The saline matter removed by water is chloride of potassium, and a considerable quantity of chloride of aluminium.

Prop.—As thus formed, it is a grey powder, very similar to that of platinum. It is generally in small scales or spangles of a metallic lustre; and sometimes small, slightly coherent, spongy masses are observed, which in some places have the lustre and white colour of tin. The same appearance is rendered perfectly distinct by pressure on steel, or in an agate mortar; so that the lustre of aluminium is decidedly metallic. In its fused state it is a conductor of electricity, though it does not possess this property when in the form of powder. This remark, of a metal conducting the electric fluid in one state and not in another, is very instructive; and Wöhler observed an instance of the same kind in iron, which in the state of fine powder is a non-conductor of electricity.

Aluminium requires for fusion a temperature higher than that at which cast iron is liquefied. When heated to redness in the open air, it takes fire and burns with vivid light, yielding aluminous earth of a white colour, and of considerable hardness. Sprinkled in powder in the flame of a candle, brilliant sparks are emitted, like those given off during the combustion of iron in oxygen gas. When heated to redness in a vessel of pure oxygen gas, it burns with an exceedingly vivid light, and emission of intense heat. The resulting alumina is partially vitrified, of a yellowish colour, and equal in hardness to the native crystallized aluminous earth, corundum. Heated to near redness in an atmosphere of chlorine, it takes fire, and chloride of aluminium is sublimed.

Aluminium is not oxidized by water at common temperatures, nor is its lustre tarnished by lying in water during its evaporation. On heating the water to near its boiling point, oxidation of the metal commences, with feeble disengagement of hydrogen gas, the evolution of which continues even long after cooling, but at length wholly ceases. The oxidation, however, is very slight; and even after continued ebullition, the smallest particles of aluminium appear to have suffered scarcely any change.

It is not attacked by concentrated sulphuric or nitric acid at common temperatures. In the former, with the aid of heat, it is rapidly dissolved with disengagement of sulphurous acid gas. In dilute hydrochloric and sulphuric acid, and also in a dilute solution of potassa, it dissolves with evolution of hydrogen gas. Ammonia produces a similar effect, and dissolves a large quantity of alumina. The hydrogen gas which makes its appearance is of course derived from water, the oxygen of which combines with the metal so as to constitute alumina.

From the composition of the sulphates of alumina, ascertained by Berzelius, Stromeyer, and Phillips, the equivalent of alumina may be estimated either at 25·7, or at 51·4, twice that number. Now chemists have no direct means of discovering the atomic constitution of alumina, inasmuch as aluminium combines with oxygen and most other elements in one proportion only. Thomson assumes alumina to consist of single atoms of its elements: but most chemists, seeing that alumina has little analogy to protoxides in its modes of combining, but that in its form and all its chemical relations it closely resembles peroxide of iron, have inferred that the simplest molecule of alumina contains 2 atoms of aluminium and 3 atoms of oxygen. On this supposition 51·4 must be the eq. of alumina, and 13·7 that of aluminium; its symb. Al. The composition of its compounds described in this section is the following:—

2 eq.	Aluminium.		Equiv.	Formulæ.
Sesquioxide .	27·4+Oxygen	24	3 eq.= 51·4	$2Al+3O$ or Al_2O_3.
Sesquichloride .	27·4+Chlorine	106·26	3 eq.=132·66	$2Al+3Cl$ or Al_2Cl_3.
Sesquisulphuret .	27·4+Sulphur	48·3	3 eq.= 74·7	$2Al+3S$ or Al_2S_3.
Sesquiphosphuret	27·4+Phosphs.	47·1	3 eq.= 73·5	$2Al+3P$ or Al_2P_3.
Sesquiseleniuret .	27·4+Selenium	118·2	3 eq.=144·6	$2Al+3Se$ or Al_2Se_3.

The composition of the last four compounds is matter of inference from the change which they respectively undergo by the action of water.

Sesquioxide of Aluminium.—Hist. and Prep.—The only known oxide of this metal, and is commonly called *alumina* or *aluminous earth.* It is one of the most abundant productions of nature. It is found in every region of the globe, and in rocks of all ages, being a constituent of the oldest primary mountains, of the secondary strata, and of the most recent alluvial depositions. The different kinds of clay of which bricks, pipes, and earthenware are made, consist of hydrate of alumina in a greater or less degree of purity. Though this earth commonly appears in rude amorphous masses, it is sometimes found beautifully crystallized.—The ruby and the sapphire, two of the most beautiful gems with which we are acquainted, are composed almost solely of alumina.

Pure alumina is prepared from alum, sulphate of alumina, and potassa. This salt, as purchased in the shops, is frequently contaminated with peroxide of iron, and consequently unfit for many chemical purposes; but it may be separated from this impurity by repeated crystallization. Its absence is proved by the alum being soluble without residue in a solution of pure potassa; whereas, when peroxide of iron is present, it is either left undissolved in the first instance, or deposited after a few hours in yellowish-brown flocks. Any quantity of purified alum is dissolved in four or five times its weight of boiling water, a slight excess of carbonate of potassa added, and after digesting for a few minutes, the bulky hydrate of alumina is collected on a filter, and well washed with hot water. It is necessary in this operation to digest and employ an excess of alkali; since otherwise the precipitate would retain some sulphuric acid in the form of a subsulphate. But the alumina, as thus prepared, is not yet quite pure; for it retains some of the alkali with such force, that it cannot be separated by the action of water. For this reason the precipitate must be re-dissolved in dilute hydrochloric acid, and thrown down by means of pure ammonia or its carbonate. This precipitate, after being well washed and exposed to a white heat, yields pure anhydrous alumina. Ammonia cannot be employed for precipitating aluminous earth directly from alum, because sulphate of alumina is not completely decomposed by this alkali. (Berzelius.) Liebig precipitates alum with an excess of chloride of barium, evaporates the filtered liquid to dryness, and ignites the residue. Water now dissolves the chlorides of potassium and barium, and leaves alumina as a white powder, very easily washed. This is a great improvement, for the washing of the hydrate, in the process first described, is a most tedious operation. A still easier process, proposed by Gay-Lussac, is to expose sulphate of alumina and ammonia to a strong heat, so as to expel the ammonia and sulphuric acid.

Prop.—Alumina has neither taste nor smell, and is quite insoluble in water. It is very infusible, though less so than lime or magnesia. It has a powerful affinity for water, attracting moisture from the atmosphere with avidity; and, for a like reason, it adheres tenaciously to the tongue when applied to it. Mixed with a due proportion of water, it yields a soft cohesive mass, susceptible of being moulded into regular forms, a property upon which depends its employment in the art of pottery. When once moistened, it cannot be rendered anhydrous, except by exposure to a full white heat; and in proportion as it parts with water, its volume diminishes. Owing to its insolubility, it does not affect the blue colour of plants. It appears to possess the properties both of an acid and of an alkali:—of an acid, by uniting with alkaline basis, such as potassa, lime, and baryta;—and of an alkali, by forming salts with acids. In neither case, however, are its soluble compounds neutral with respect to test paper.

Alumina most probably forms several different hydrates with water, and two have been described by Thomson. One of these, apparently composed of 6 eq. of water to 1 of alumina, so that its formula is $Al_2O_3 + 6$ aq., was procured by exposing precipitated alumina for the space of two months to a dry air, the temperature of which did not exceed 60°. The other is a terhydrate prepared by drying the preceding at a heat of about 100°, and its formula is therefore $Al_2O_3 + 3$ aq. The mineral called Gibbsite has a similar composition.

Alumina is easily recognized by the following characters:—1. It is separated from acids, as a hydrate, by all the alkaline carbonates and by pure ammonia. 2. It is precipitated by pure potassa or soda, but the precipitate is completely re-dissolved by an excess of the alkali.

Its eq. is 51·4; symb. $2Al + 3O$, $\overset{\cdots}{\underline{Al}}$, or Al_2O_3.

Sesquichloride of Aluminium.—Hist.—Oersted discovered this compound by transmitting dry chlorine gas over a mixture of alumina and charcoal heated to redness. By acting on this substance with an amalgam of potassium, and expelling the mercury by heat, he obtained metallic matter, which he believed to be aluminium; but not having leisure to pursue the inquiry himself, he requested Wöhler to investigate the subject. Wöhler did not arrive at any satisfactory conclusion by the method suggested by Oersted; but met with complete success by means of pure potassium, as already described.

Prep.—To procure chloride of aluminium, Wöhler precipitated aluminous earth from a hot solution of alum by means of potassa, and mixed the hydrate, when dry, with pulverized charcoal, sugar, and oil, so as to form a thick paste, which was heated in a covered crucible until all the organic matter was destroyed. By this means the alumina was brought into a state of intimate mixture with finely-divided charcoal, and while yet hot was introduced into a tube of porcelain, fixed in a convenient furnace. After expelling atmospheric air from the interior of the apparatus by a current of dry chlorine gas, the tube was brought to a red heat. The formation of chloride of aluminium then commenced, and continued, with disengagement of carbonic oxide gas, during an hour and a half, when the tube became impervious from sublimed chloride of aluminium collected within it. The process was then necessarily discontinued.

Prop.—As thus formed, chloride of aluminium is of a pale greenish-yellow colour, partially translucent, and of a highly crystalline lamellated texture, somewhat like talc, but without regular crystals. On exposure to the air, it fumes slightly, emits an odour of hydrochloric acid gas, and, deliquescing, yields a clear liquid. When thrown into water, it is speedily dissolved with a hissing noise; and so much heat is evolved, that the water, if in small quantity, is brought into a state of brisk ebullition. The solution is a true hydrochlorate of alumina, formed by decomposition of water; for, when gently evaporated, hydrochloric acid escapes, and alumina is gradually deposited. According to Oersted it is volatile at a temperature a little higher than 212°, and fuses nearly at the same degree.

Sesquisulphuret of Aluminium.—Sulphur may be distilled from aluminium without combining with it; but if a piece of sulphur is dropped on aluminium when strongly incandescent, so that it may be enveloped in an atmosphere of the vapour of sulphur, the union is effected with vivid emission of light. The resulting sulphuret is a partially vitrified, semi-metallic mass, which acquires an iron-black metallic lustre when burnished. Applied to the tongue, it excites a pricking warm taste of hydrosulphuric acid. When put into pure water, or on exposure to the air, it is resolved, by an interchange of elements, into alumina and hydrosulphuric acid, the latter escaping as gas. It is to be presumed that

$$\underset{Al_2S_3}{\text{1 eq. Sulphuret}} \text{ and } \underset{3HO}{\text{3 eq. Water}} \text{ yield } \underset{Al_2O_3}{\text{1 eq. Alumina}} \text{ and } \underset{3HS.}{\text{3 eq. Hydrosulph. Acid.}}$$

Wöhler finds that sulphuret of aluminium cannot be generated by the action of hydrogen gas on sulphate of alumina at a red heat; for in that case all the acid is expelled, without the aluminous earth being reduced.

Sesquiphosphuret of Aluminium.—When aluminium is heated to redness in contact with the vapour of phosphorus, it takes fire, and emits a brilliant light. The product is described by Wöhler as a blackish-grey pulverulent mass, which by friction acquires a dark grey metallic lustre, and in the air smells instantly of phosphuretted hydrogen. By the action of water alumina and phosphuretted hydrogen gas are generated, but the latter is not spontaneously inflammable. The effervescence is less rapid than with the sulphuret, but is increased by heat.

Sesquiseleniuret of Aluminium.—This compound is formed, with disengagement of heat and light, by heating to redness a mixture of selenium and aluminium. The product is black and pulverulent, and assumes a dark metallic lustre when rubbed. In the air it emits a strong odour of hydroselenic acid; and this gas is rapidly disengaged by the action of water, which is speedily reddened by the separation of selenium.

SECTION IX.

GLUCINIUM, YTTRIUM, THORIUM, ZIRCONIUM.

GLUCINIUM.

Glucina, which was discovered by Vauquelin in the year 1798, has hitherto been found only in three rare minerals, the euclase, beryl, and emerald. It is the only oxide of a metal which Wöhler succeeded in preparing in the year 1828 by a process exactly similar to that described in the last section. Chloride of glucinium is readily attacked by potassium when heated with the flame of a spirit-lamp, and the decomposition is attended with intense heat. After removing the resulting chloride of potassium by cold water, the glucinium appears in the form of a greyish-black powder, which acquires a dark metallic lustre by burnishing. It may be exposed to air and moisture, or be even boiled in water, without oxidation. When heated in the open air, it takes fire and burns with a most vivid light; and in oxygen gas the combustion is attended with extraordinary splendour. The product in both cases is glucina, which is not at all fused by the intense heat that accompanies its formation. The metal is readily oxidized and dissolved in sulphuric, nitric, or hydrochloric acid with the aid of heat; and the same ensues, with disengagement of hydrogen gas, in solution of potassa. It is not attacked, however, by pure ammonia. When moderately heated in chlorine gas, it burns with great splendour, and a crystallized chloride sublimes. Similar phenomena ensue in the vapour of bromine and iodine; and it unites readily with sulphur, selenium, phosphorus, and arsenic. (Phil. Mag. and Annals, v. 392.)

According to the experiments of Berzelius, glucina contains 31·154 per cent. of oxygen, and consequently its eq. is 26·5 on the supposition that its constitution is similar to that of alumina, with which it is closely associated both in nature and in many of its properties. Its symb. is G.

Oxide of Glucinium or Glucina.—Prep.—This oxide is commonly prepared from beryl, in which it exists to the extent of about 14 per cent. combined with silicic acid and alumina. In order to procure it in a separate state, the mineral is reduced to an exceedingly fine powder, mixed with three times its weight of carbonate of potassa, and exposed to a strong red heat for half an hour, so that the mixture may be fused. The mass is then dissolved in dilute hydrochloric acid, and the solution evaporated to perfect dryness; by which means the silicic acid is rendered quite insoluble. The alumina and glucina are then redissolved in water acidulated with hydrochloric acid, and thrown down together by pure ammonia. The precipitate, after being well washed, is macerated with a large excess of carbonate of ammonia, by which glucina is dissolved; and on boiling the filtered liquid, carbonate of glucina subsides. By means of a red heat its carbonic acid is entirely expelled.

Another process has been recommended by Berthier, who directs the beryl to be mixed in fine powder with its own weight of marble, and the mixture to be exposed in a crucible to a strong heat. In this manner a glass is obtained, which when in fine powder is attacked freely by hydrochloric or sulphuric acid. From this solution the glucina may be obtained as before.

Prop.—Glucina is a white powder, which has neither taste nor odour, and is quite insoluble in water. Its sp. gr. is 3. Vegetable colours are not affected by it. The salts which it forms with acids have a sweetish taste, a circumstance which distinguishes glucina from other earths, and from which its name is derived (from *γλυϰυς*, sweet).

Glucina may be known chemically by the following characters:—1. Pure potassa or soda precipitates glucina from its salts, but an excess of the alkali redissolves it. 2. It is precipitated permanently by pure ammonia as a hydrate, and by fixed alkaline carbonates as a carbonate of glucina. 3. It is dissolved completely by a cold solution of carbonate of ammonia, and is precipitated from it by boiling. By means of this property, glucina may be both distinguished and separated from alumina.

Its eq. is 77; symb. $2G + 3O$, $\overset{\cdots}{G}$, or G_2O_3.

YTTRIUM.

Yttrium is the metallic base of an earth which was discovered in the year 1794 by Professor Gadolin, in a mineral found at Ytterby, in Sweden, from which it received the name of *Yttria*. The metal itself was prepared by Wöhler in 1828 by a process similar to that above described. Its texture, by which it is distinguished from glucinium and aluminium, is scaly, its colour greyish-black, and its lustre perfectly metallic. In colour and lustre it is inferior to aluminium, bearing in these respects nearly the same relation to that metal, that iron does to tin. It is a brittle metal, while aluminium is ductile. It is not oxidized either in air or water; but when heated to redness, it burns with splendour even in atmospheric air, and with far greater brilliancy in oxygen gas. The product, yttria, is white, and shows unequivocal marks of fusion. It dissolves in sulphuric acid, and also, though less readily, in solution of potassa; but it is not attacked by ammonia. It combines with sulphur, selenium, and phosphorus. (Phil. Mag. and Annals, v. 393.)

The salts of yttria have in general a sweet taste, and the sulphate and several others have an amethyst colour; but the recent researches of Mosander have shown that this is owing to the presence of one or both of the new metals, Erbium and Terbium, which he finds to be commonly associated with yttrium. It is precipitated as a hydrate by the pure alkalies, and is not redissolved by an excess of the precipitant; but alkaline carbonates, especially that of ammonia, dissolve it in the cold, though less freely than glucina, and carbonate of yttria is precipitated by boiling. Of all the earths, it bears the closest resemblance to glucina; but it is readily distinguished from it by the colour of its sulphate, by its insolubility in pure potassa, and by yielding a precipitate with ferrocyanuret of potassium (Berzelius). The eq. of yttrium, as deduced by Berzelius, is 32·2; and that of yttria, which is probably a protoxide, is 40·2. But as we have reason to doubt whether absolutely pure yttria has yet been obtained, these numbers must be regarded only as approximations.

The symb. of the metal is Y; of its oxide $Y + O$, $\dot{Y}$, or YO.

TERBIUM. ERBIUM.

Terbium and Erbium (derived like yttrium, from Ytterby, the locality where the mineral Gadolinite occurs) are the names given by Mosander to two new metals, the oxides of which accompany yttria. When the solution of a salt of yttrium, as hitherto prepared, is mixed with successive small portions of alkali, a series of precipitates is obtained; of which the first, when heated to redness, becomes yellow or orange, the succeeding ones exhibit, when heated, a paler yellow, approaching to white, and the last remain quite white when ignited. These latter appear to be pure oxide of yttrium; while the first precipitates are composed chiefly of oxide of erbium with oxide of terbium and yttrium, and, in the intermediate ones, oxide of terbium predominates. Those precipitates which become yellow when heated form red salts, but the pure yttria forms salts which are colourless.

Oxide of erbium appears to be the weakest base of the three. It is yellow or orange yellow, and gives red salts. Oxide of terbium seems to be colourless when pure, but its salts have a pale red tint. The nitrate of terbium is permanent except in a very damp atmosphere, while the nitrate of yttria is highly deliquescent. Sulphate of terbium is efflorescent, but sulphate of yttria is quite permanent. These characters serve to distinguish terbium from yttrium, and erbium is easily recognized by the colour of its compounds.

For further details I must refer to Mosander's paper in Berzelius's Jahresbericht. (German edition, xxiii. 144.) Mosander has made it quite certain that perfectly pure yttria has not yet been described; but he has not yet been able to give a satisfactory method of separating the above three metals from each other, so that the pure oxides of erbium and terbium are equally unknown. For this reason I have treated them very briefly, and have said nothing of their equivalents, which cannot yet be ascertained.

THORIUM.

The earthy substance formerly called *thorina* was found by Berzelius to be phosphate of yttria; but in 1828 he discovered a new earth, so similar in some respects to what was formerly called thorina, that he applied this term to the new substance. The metallic base of thorina (thorium) was procured by the action of potassium on chloride of thorium, the decomposition being accompanied with a slight detonation. On washing the mass, thorium is left in the form of a heavy metallic powder, of a deep leaden-grey colour; and when pressed in an agate mortar, it acquires metallic lustre and an iron-grey tint. Thorium is not oxidized either by hot or cold water; but when gently heated in the open air, it burns with great brilliancy, comparable to that of phosphorus burning in oxygen. The resulting thorina is as white as snow, and does not exhibit the least trace of fusion. It is not attacked by caustic alkalies at a boiling heat; is scarcely at all acted on by nitric acid, and very slowly by the sulphuric, but it is readily dissolved with disengagement of hydrogen gas by hydrochloric acid.

Thorina.—Hist. and Prep.—Procured from a rare Norwegian mineral, now called *thorite*, which was sent to Berzelius by Esmark. It constitutes 57·91 per cent. of the mineral, and occurs in the form of a hydrated silicate of thorina. In order to prepare thorina, the mineral is reduced to powder, and digested in hydrochloric acid; when a gelatinous mass is formed, from which silicic acid is separated by evaporating to dryness, and dissolving the soluble parts in dilute acid. The solution is then freed from lead and tin, which occur in thorina along with several impurities, by hydrosulphuric acid, and the earths are thrown down by pure ammonia. The precipitate, after being well washed, is dissolved in dilute sulphuric acid, and the solution evaporated at a high temperature till only a small quantity of fluid remains. During the evaporation the greater part of the thorina is deposited as a sulphate; and on decanting the remaining fluid, washing the residue, and heating it to redness, pure thorina remains. (An. de Ch. et Ph. xliii. 5.)

Prop.—Thorina, when formed by the oxidation of thorium, or after being strongly heated, is a white earthy substance, of sp. gr. 9·402, and insoluble in all the acids except the sulphuric; and it dissolves even in that with difficulty. It is precipitated from its solutions by the caustic alkalies as a hydrate, and in this state absorbs carbonic acid from the atmosphere, and dissolves readily in acids. All the alkaline carbonates dissolve the hydrate, carbonate, and sub-salts of thorina. Its exact composition is not known; but its eq. is about 67·6.

Thorina is distinguished from alumina and glucina by its insolubility in pure potassa; from yttria by forming with sulphate of potassa a double salt which is quite insoluble in a cold saturated solution of sulphate of potassa; and from zirconia by the circumstance that this earth, after being precipitated from a hot solution of sulphate of potassa, is almost insoluble in water and the acids. Thorina is precipitated, also, by ferrocyanuret of potassium, which does not separate zirconia from its solutions. Berzelius has remarked that sulphate of thorina is much more soluble in cold than in hot water, so that a cold saturated solution becomes turbid when heated, and in cooling recovers its transparency.

Chloride of thorium is readily prepared by carbonizing an intimate mixture of thorina and sugar in a covered platinum crucible, and then exposing the residue at a red heat in a porcelain tube to a current of dry chlorine. The chloride, possessing but little volatility, collects in the tube just beyond the ignited part in the form of a partially fused, crystalline, white mass. It is soluble in water with considerable rise of temperature.

When thorium is heated in the vapour of sulphur, the phenomena of combustion ensue with the same brilliancy as in air, and a sulphuret results. A phosphuret may be formed by a similar process.

ZIRCONIUM.

Hist. and Prep.—The experiments of Davy proved zirconia to be an oxidized body, and afforded a presumption that its base, *zirconium*, is of a metallic nature; but Berzelius first obtained the metal in 1824 by heating with a spirit-lamp a mixture of potassium and the double fluoride of zirconium and potassium, carefully dried in a tube of glass or iron. The reduction takes place at a temperature below redness, without emission of light; and the mass is washed with boiling water, and afterwards digested for some time in dilute hydrochloric acid. The residue is pure zirconium.

Prop.—Zirconium, thus obtained, is in the form of a black powder, which may be boiled in water without being oxidized, and is attacked with difficulty by sulphuric, hydrochloric, or nitrohydrochloric acids; but it is dissolved readily, and with disengagement of hydrogen gas, by hydrofluoric acid. Heated in the open air, it takes fire at a temperature far below incandescence, burns brightly, and is converted into zirconia. Its metallic nature seems somewhat questionable. It may indeed be pressed out into thin shining scales of a dark grey colour, and of a lustre which may be called metallic; but its particles cohere together very feebly, and it has not been procured in a state capable of conducting electricity. These points, however, require further investigation before a decided opinion on the subject can be adopted. (Pog. Annalen, iv.)

Oxide of Zirconium, or *Zirconia*, was discovered in the year 1789 by Klaproth in the Jargon or Zircon of Ceylon, and has since been found in the Hyacinth from Expailly in France. Scheerer prepares zirconia by fusing levigated zircons with four parts of carbonate of soda. From the fused mass, water removes silicate and carbonate of soda, along with flocks of oxide of iron and manganese, and leaves a heavy white sandy powder, a compound of soda with zirconia. When hydrochloric acid is poured on this powder, it swells up, heat being developed, and on the addition of water after a certain time, a clear solution is obtained, from which ammonia precipitates pure snow-white zirconia. It is an earthy substance, resembling alumina in appearance, of sp. gr. 4·3, having neither taste nor odour, and quite insoluble in water. It is so hard that it will scratch glass. Its colour, when pure, is white; but it has frequently a tinge of yellow, owing to the presence of iron, from which it is separated with great difficulty. It phosphoresces vividly when heated strongly before the blow-pipe. Its salts are distinguished from those of alumina or glucina by being precipitated by all the pure alkalies, in an excess of which it is insoluble. The alkaline carbonates precipitate it as carbonate of zirconia, and a small portion of it is redissolved by an excess of the precipitant, especially when a bicarbonate is employed. It differs from all the earths, except thorina, in being precipitated when any of its neutral salts are boiled with a saturated solution of sulphate of potassa, the zirconia subsiding as a subsalt, and the potassa remaining in solution as a bisulphate. Zirconia is precipitated from its salts by pure ammonia as a bulky hydrate, which is readily soluble in acids ; but if this hydrate is ignited, dried, or even washed with boiling water, it afterwards resists the action of the acids, and is dissolved by them with great difficulty. Strong sulphuric acid is then its best solvent (Berzelius). When hydrated zirconia is heated to commencing redness, it parts with its water, and soon after emits a very vivid glow for a short time. This phenomenon appears to depend upon the particles of the zirconia suddenly approaching each other, and thus acquiring much greater density than it previously possessed. Oxide of chromium, titanic acid, and several other compounds afford instances of the same appearance ; and whenever it takes place, the susceptibility of the substance to be attacked by fluid reagents is greatly diminished (Berzelius).

The composition of zirconia has not yet been satisfactorily determined. From some analyses by Berzelius, described in the Essay above referred to, it is probable that the eq. of this earth is about 33·7 ; its symb. $2Zr + 3O$, $\overset{\cdots}{\underline{Z}r}$, or $Zr_2 O_3$.

Sulphuret of Zirconium.—This compound may be prepared, according to Berzelius, by heating zirconium with sulphur in an atmosphere of hydrogen gas ; and the union is effected with feeble mission of light. The product is pulverulent, a non-conductor of electricity, of a dark chesnut-brown colour, and without lustre. It is insoluble in sulphuric, nitric, and hydrochloric acid ; and it is slowly attacked by nitro-hydrochloric acid, even with the aid of heat. It is readily dissolved by hydrofluoric acid, with disengagement of hydrogen gas.

Norium.—Swanberg has very recently announced that the zircons of Norway contain, besides zirconia, a new earth, Noria, or oxide of norium, which differs from zirconia in several particulars, although very analogous to it, and has a lower atomic weight. It is said to occur also, but in smaller proportion, in the zircons of Ceylon and in those of Expailly.

The same chemist states that the zirconia extracted from the mineral Eudialite contains, besides oxide of cerium and the other oxides which accompany it, two other oxides, to which no name has yet been given. One of them resembles yttria, but has a lower atomic weight. The other has a yellow colour which is destroyed by heat. We must wait for more details concerning these oxides.

CLASS II.

METALS, THE OXIDES OF WHICH ARE NEITHER ALKALIES NOR EARTHS.

ORDER I.

METALS WHICH DECOMPOSE WATER AT A RED HEAT.

SECTION X.

MANGANESE.

Hist. and Prep.—The black oxide of manganese was described in the year 1774 by Scheele as a peculiar earth, and Gahn subsequently showed that it contains a new metal, to which he gave the name of *magnesium ;* a term since applied to the metallic base of magnesia, and for which the words *manganesium* and *manganium* have been substituted. This metal, owing doubtless to its strong affinity for oxygen, has never been found in an uncombined state in the earth ; but its oxides are very abundant. The metal may be obtained by forming finely powdered oxide of manganese into a paste with oil, laying the mass in a hessian crucible lined with charcoal, luting down a cover carefully, and exposing it during an hour and a half, or two hours, to the strongest heat of a smith's forge.

Prop.—A hard brittle metal, of a greyish-white colour, and granular texture. Its sp. gr. according to John, is 8·013. When pure it is not attracted by the magnet, but Berthier has lately stated that it possesses this property at very low temperatures. It is exceedingly infusible, requiring the highest heat of a wind furnace for fusion. It soon tarnishes on exposure to the air, and absorbs oxygen with rapidity when heated to redness in open vessels. It slowly decomposes water at common temperatures with disengagement of hydrogen gas ; but at a red heat decomposition is rapid, and protoxide of manganese is generated. Decomposition of water is likewise occasioned by dilute sulphuric acid, and sulphate of protoxide of manganese is the product.

Berzelius, from an analysis of chloride of manganese, found 27·7 as the eq. of manganese, a number which agrees closely with my own experiments on the same chloride. Its symb. is Mn. The composition of the compounds of manganese described in this section is as follows :—

	Manganese.			Equiv.	Formulæ.
Protoxide .	27·7	1 eq.+Oxygen	8	1 eq.= 35·7	$Mn+O$ or MnO.
Sesquioxide .	55·4	2 eq.+do.	24	3 eq.= 79·4	$2Mn+3O$ or Mn_2O_3.
Peroxide .	27·7	1 eq.+do.	16	2 eq.= 43·7	$Mn+2O$ or MnO_2.
Red Oxide .	83·1	3 eq.+do.	32	4 eq.=115·1	$3Mn+4O$ or Mn_3O_4.
Varvicite .	110·8	4 eq.+do.	56	7 eq.=166·8	$4Mn+7O$ or Mn_4O_7.
Mangan. Acid	27·7	1 eq.+do.	24	3 eq.= 51·7	$Mn+3O$ or MnO_3.
Permang. Acid	55·4	2 eq.+do.	56	7 eq.=111·4	$2Mn+7O$ or Mn_2O_7.
Protochloride .	27·7	1 eq.+Chlor.	35·42	1 eq.= 63·12	$Mn+Cl$ or $MnCl$.
Perchloride .	55·4	2 eq.+do.	247·94	7 eq.=303·34	$2Mn+7Cl$ or Mn_2Cl_7.
Perfluoride .	55·4	2 eq.+Fluor.	130·76	7 eq.=186·16	$2Mn+7F$ or Mn_2F_7.
Protosulphuret	27·7	1 eq.+Sulph.	16·1	1 eq.= 43·8	$Mn+S$ or MnS.

OXIDES OF MANGANESE.

In studying metallic oxides, it is necessary to distinguish oxides formed by the direct union of oxygen and a metal, from those that consist of two other oxides united with each other, and which therefore, in composition, partake of the nature of a salt rather than of an oxide. An instance of this kind of combination is supplied by the black oxide of iron ; and it is probable that two of the five compounds enumerated as oxides of manganese have a similar constitution. Their composition has been particularly investigated by Berzelius, Thomson (First Principles, i.), Arfwedson,* Berthier,† and myself.‡

Protoxide.—Prep.—By this term is meant that oxide of manganese which is a strong salifiable base, is contained in all the ordinary salts of this metal, and which appears to be its lowest degree of oxidation. This oxide may be formed by exposing the peroxide, sesquioxide, or red oxide of manganese, to the combined agency of charcoal and a white heat; or by exposing either of the oxides of manganese contained in a tube of glass, porcelain, or iron, to a current of hydrogen gas at an elevated temperature. The best material for this purpose is the red oxide prepared from nitrate of oxide of manganese; since the native oxides, especially the peroxide, are fully reduced to the state of protoxide by hydrogen with difficulty. The reduction commences at a low red heat; but to decompose all the red oxide, a full red heat is required. The same compound is formed by the action of hydrogen gas at an intense white heat. Wöhler and Liebig have shewn that the protoxide is also obtained by fusing chloride of manganese in a platinum crucible with about twice its weight of carbonate of soda, and its own weight of sal-ammoniac, and afterwards dissolving the chloride of sodium by water.

Prop.—Protoxide of manganese, when pure, is of a light green colour, very near the mountain green. According to Forchammer it attracts oxygen rapidly from the air; but in my experiments it was very permanent, undergoing no change either in weight or appearance during the space of nineteen days. At 600° it is oxidized with considerable rapidity, and at a low red heat is converted in an instant into red oxide. It sometimes takes fire when thus heated, especially when the mass is considerable. It unites readily with acids without effervescence, producing the same salts as when the same acids act on carbonate of oxide of manganese. When it comes in contact with concentrated sulphuric acid, intense heat is instantly evolved; and the same phenomenon is produced, though in a less degree, by strong hydrochloric acid. The resulting salt is the same as when these acids are heated with either of the other oxides of manganese. If quite pure, the protoxide should readily and completely dissolve in cold dilute sulphuric acid, and yield a colourless solution.

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* Letter from Berzelius in the An. de Ch. et Ph., vi. † Ibid. xx.

‡ Philos. Trans. of Edin. for 1828 ; or Phil. Mag. and Annals, iv.

In order to prepare a pure salt of manganese from the common peroxide of commerce, the following process may be employed:—The solution which remains when chlorine is made by the action of muriatic acid on peroxide of manganese is rendered neutral by gently evaporating it to dryness. A portion, which varies with the proportion of iron present, and is easily ascertained by trial on a small scale, is then precipitated by an excess of carbonate of soda, and the mixed precipitate of carbonate of manganese and peroxide of iron, well washed, is digested with the remainder of the liquid. The protoxide of manganese enters the liquid, expelling the peroxide of iron, and at last a liquid is obtained quite free from iron. It ought to give a bright flesh-coloured precipitate with hydrosulphuret of ammonia, and a white with ferrocyanide of potassium. Should the first drop of the former test cause a dark precipitate, this is owing to the presence, not of iron, but of cobalt and nickel, which, according to Gregory, are almost uniformly present in small quantity in the oxide of manganese. They are easily removed by adding the hydrosulphuret till it gives a pure flesh-coloured precipitate. If the oxide, before being dissolved in muriatic acid, has been digested in very diluted muriatic acid, and washed, no lime can be present in the solution. The iron can only escape complete precipitation if it be partly in the state of protoxide; but in preparing chlorine the iron is fully oxidized. If, however, protoxide should be present, it is readily peroxidized by boiling with a little nitric acid. This process, suggested by Everitt, is founded on the fact, that all carbonates of protoxides, when digested with solutions of peroxide of iron, precipitate the latter; and the manganese contained in the mixed solution is thus ingeniously made use of to effect its own purification. (Phil. Mag. and An. vi. 193.) Other less convenient methods, which, however, yield a pure product, have been suggested, particularly one by Faraday. (Quart. Journ. vi.)

The salts of manganese are in general colourless if quite pure; but more frequently they have a shade of pink, owing to the presence of a little red oxide or permanganic acid. The protoxide is precipitated from its solutions as a white hydrate of ammonia, or the pure fixed alkalies; as white carbonate of protoxide of manganese by alkaline carbonates and bicarbonates; and as white ferrocyanide of manganese by ferrocyanide of potassium, a character by which the absence of iron may be demonstrated. These white precipitates, with the exception of that obtained by means of a bicarbonate, very soon become brown from the absorption of oxygen. None of the salts of manganese which contain a strong acid, such as the nitric, or sulphuric, are precipitated by hydrosulphuric acid. With an alkaline hydrosulphate, on the contrary, a flesh-coloured precipitate is formed, which is a hydrated protosulphuret of manganese: when heated in close vessels, it yields a dark-coloured sulphuret, and water is evolved.

Its eq. is 35·7; symb. $Mn + O, \dot{M}n$, or MnO.

Sesquioxide.—Hist. and Prep.—This oxide occurs nearly pure in nature, and as a hydrate it is found abundantly, often in large prismatic crystals, at Ihlefeld in the Hartz. It may be formed artificially by exposing peroxide of manganese for a considerable time to a moderate red heat, and therefore is the chief residue of the usual process for procuring a supply of oxygen gas; but it is difficult so to regulate the degree and duration of the heat, that the resulting oxide shall be quite pure.

Prop.—The colour of the sesquioxide of manganese varies with the source from which it is derived. That which is procured by means of heat from the native peroxide or hydrated sesquioxide, has a brown tint; but when prepared from nitrate of oxide of manganese, it is nearly as black as the peroxide, and the native sesquioxide is of the same colour. With sulphuric and hydrochloric acids it gives rise to the same phenomenon as the peroxide, but of course yields a smaller proportional quantity of oxygen and chlorine gases. It is more easily attacked than the peroxide by cold sulphuric acid. With strong nitric acid it yields a soluble protonitrate and the peroxide, and when boiled with dilute sulphuric acid, it undergoes a similar change. From the proportion of oxygen and manganese in this oxide, it has sometimes been regarded as a compound of 43·7 parts or 1 eq. of peroxide, and 35·7 parts or 1 eq. of protoxide of manganese. In that case the sesquioxide would be constituted like a salt, and should have the properties of that class of compounds; but Mitscherlich has succeeded in combining it with sulphuric acid, and has obtained with it an alum similar in form and constitution to those of peroxide of iron and alumina. It must therefore be considered as a direct compound of 2 eq. of manganese and 3 eq. of oxygen.

Its eq. is 79·4; symb. $2Mn+3O$,Mn, or Mn_2O_3.

Peroxide.—Hist. and Prep.—The well known ore commonly called, from its colour, black oxide of manganese. It generally occurs massive, of an earthy appearance, and mixed with other substances, such as siliceous and aluminous earths, oxide of iron, and carbonate of lime. It is sometimes found, on the contrary, in the form of minute prisms grouped together, and radiating from a common centre. In these states it is anhydrous; but the essential ingredient of one variety of the earthy mineral called *wad* is hydrated peroxide of manganese, consisting of 1 eq. of water and 2 of the oxide. The peroxide may be made artificially by exposing nitrate of oxide of manganese to a commencing red heat, until the whole of the nitric acid is expelled; but I have never succeeded in procuring it quite pure by this process, because the heat required to drive off the last traces of acid likewise expels some oxygen from the peroxide. The hydrated peroxide, containing 1 eq. of water and one of oxide, is formed by precipitating the protochloride of manganese by chloride of lime; and the same compound results from the decomposition of the acids of manganese, either in water or by dilute acid.

Prop.—Not changed by exposure to the air, is insoluble in water, and does not unite either with acids or alkalies. When boiled with sulphuric acid, it yields oxygen gas, and a sulphate of the protoxide is formed. With hydrochloric acid, chloride of manganese is generated, and chlorine is evolved. The solution in both cases is of a deep-red colour, provided undissolved oxide is present; but if separated from the undissolved portions, it is readily rendered colourless by heat. The colour is commonly attributed to a small quantity of the sesquioxide or red oxide of manganese dissolved by the free acid; but Mr. Pearsall, of Hull, has gone far to prove that it is owing to the presence of permanganic acid. (R. Inst. Journal, N. S., No. iv. 49.) The action of sulphuric acid in the cold is exceedingly tardy and feeble, a minute quantity of oxygen gas is slowly disengaged, and the acid acquires an amethyst-red tint. On exposure to a red heat, it is converted, with evolution of oxygen gas, into the sesquioxide of manganese.

Peroxide of manganese is employed in the arts, in the manufacture of glass, and in preparing chlorine for bleaching. In the laboratory it is used for procuring chlorine and oxygen gases, and in the preparation of the salts of manganese.

Its eq. is 43·7; symb. $Mn + 2O, \ddot{Mn}$, or MnO_3.

Red Oxide.—The substance called red oxide of manganese, *Oxidum Manganoso-Manganicum* of Arfwedson, occurs as a natural production, and may be formed artificially by exposing the peroxide or sesquioxide to a white heat either in close or open vessels. It is also produced by absorption of oxygen from the atmosphere when the protoxide is precipitated from its salts by pure alkalies, or when the anhydrous protoxide or carbonate is heated to redness. It is very permanent in the air, not passing to a higher stage of oxidation at any temperature. Its colour when rubbed to the same degree of fineness is brownish-red when cold, and nearly black while warm. Fused with borax or glass it communicates a beautiful violet tint, a character by which manganese may be easily detected before the blowpipe; and it is the cause of the rich colour of the amethyst. It is acted on by strong sulphuric and hydrochloric acids, with the aid of heat, in the same manner as the peroxide and sesquioxide, but of course yields proportionally a smaller quantity of oxygen and chlorine gases. By cold concentrated sulphuric acid it is dissolved in small quantity without appreciable disengagement of oxygen gas, and the solution is promoted by a slight increase of temperature. The liquid has an amethyst tint, which disappears when heat is applied, or by the action of deoxidizing substances, such as protochloride of tin, or sulphurous and phosphorous acids, sulphate of protoxide of manganese being generated. By strong nitric acid, or when boiled with dilute sulphuric acid, it undergoes the same kind of change as the sesquioxide.

It may be doubted whether the red oxide is not rather a kind of salt composed of two other oxides, than a direct compound of manganese and oxygen. From the ratio of its elements it may consist either of

Sesquioxide .	79·4 or 1 equiv.	or	Peroxide .	43·7 or 1 equiv.
Protoxide .	35·7 or 1 equiv.		Protoxide .	71·4 or 2 equiv.
	115·1			115·1

It contains 27·586 per cent. of oxygen, and loses 6·896 per cent. when converted into the green oxide. Its eq. is 115·1; its symb. either $MnO + Mn_2O_3$, or $2MnO + MnO_2$.

Varvicite.—This compound is known only as a natural production, having been first noticed a few years ago by Mr. Phillips among some ores of manganese found at Hartshill, in Warwickshire. The locality of the mineral suggested its name; but I have also detected it as the constituent of an ore of manganese from Ihlefeld, sent me by Professor

Stromeyer. Varvicite was at first mistaken for peroxide of manganese, to which in the colour of its powder it bears considerable resemblance; but it is readily distinguished from that ore by its stronger lustre, greater hardness, more lamellated texture, which is very similar to that of manganite, and by yielding water freely when heated to redness. Its sp. gr. is 4·531. It has not been found regularly crystallized; but my specimen from Ihlefeld is in *pseudo-crystals*, possessing the form of the six-sided pyramid of calcareous spar. When strongly heated it is converted into red oxide, losing 5·725 per cent. of water, and 7·385 of oxygen. It is probably, like the red oxide, a compound of two other oxides; and the proportions just stated justify the supposition that it consists of 2 eq. of peroxide and 1 of sesquioxide of manganese, united in the mineral with an eq. of water. (Phil. Mag. and Annals, v. 209, vi. 281, and vii. 284.)

It has been inferred from some experiments of Berzelius and John, that there are two other oxides of manganese, which contain less oxygen than the green or protoxide. We have no proof, however, of the existence of such compounds.

Its eq. is 166·8; sym. probably $Mn_2O_3 + 2MnO_2$.

Manganic Acid.—Hist. and Prep.—Manganese is one of those metals which is capable of forming an acid with oxygen. Manganate of potassa is generated when hydrate or carbonate of potassa is heated to redness with peroxide of manganese; and nitre may be used successfully, provided the heat be high enough to decompose the nitrite of potassa. The materials absorb oxygen from the air when fused in open vessels; but manganate of potassa is equally well formed in close vessels, one portion of oxide of manganese then supplying oxygen to another. The product has been long known under the name of *mineral chameleon*, from the property of its solution to pass rapidly through several shades of colour: on the first addition of cold water a green solution is formed, which soon becomes blue, purple, and red; and ultimately a brown flocculent matter, hydrated peroxide of manganese, subsides, and the liquid becomes colourless. These changes, which are more rapid by dilution with hot water, have been successively elucidated by Chevillot and Edwards, Forchammer and Mitscherlich. (An. de Ch. et Ph., viii., and xlix. 113; and An. of Phil. xvi.)

Prop.—The phenomena above-mentioned are owing to the formation of manganate of potassa of a green colour, and to its ready conversion into the red permanganate of potassa, the blue and purple tints being due to a mixture of these compounds. Manganic acid itself cannot be obtained in an uncombined state, because it is then resolved into the hydrated peroxide and oxygen, a property which Mitscherlich availed himself of in analyzing this acid; but Mitscherlich has proved that it is analogous in composition to sulphuric acid, and its salts isomorphous with the sulphates. Manganate of potassa is obtained in crystals by forming a concentrated solution of mineral chameleon in cold water, very pure and free from carbonic acid, allowing it to subside in a stoppered bottle, and evaporating the clear green solution in vacuo with the aid of sulphuric acid. All contact of paper and other organic matter must be carefully avoided, since they deoxidize the acid, and the process should be conducted in a cool apartment. The crystals are anhydrous, and permanent in the dry state; but in solution the carbonic acid of the air suffices to decompose the acid; and even simple dilution with cold water has this effect. Mixed with a solution of potassa the manganate may be crystallized a second time in vacuo without change.

Its eq. is 51·7; symb. $Mn + 3O, \dddot{Mn}$, or MnO_3.

Permanganic Acid.—Prep.—Permanganate of potassa is obtained by heating a solution of mineral chameleon, however prepared. A better process has been indicated by Wöhler (Pog. An. xxvii. 626): it consists in fusing chlorate of potassa in a platinum crucible, and then adding peroxide of manganese in fine powder. An improvement on this has been proposed by Gregory (Lieb. An. xv. 237): he recommends 4 parts of peroxide of manganese to be mixed in fine powder with 3½ parts of chlorate of potassa, and then added to 5 parts of hydrate of potassa dissolved in a small quantity of water. The whole is evaporated to perfect dryness, powdered, and exposed in a platinum crucible to a low red heat. The mass, which has not been fused, is again powdered, and added to a large quantity of boiling water, which when clear is decanted from the sediment of peroxide of manganese, rapidly concentrated and allowed to crystallize. The crystals are at first small and almost black; but by washing with a little cold water, and solution in the smallest possible quantity of boiling water, they are obtained in very fine crystals. By the above process, this interesting salt, which has been used as an oxidising agent in various researches of organic chemistry, may be obtained in any quantity that may be desired. The acid may be obtained by adding to a solution of permanganate of baryta a quantity of bilute sulphuric acid exactly sufficient for precipitating the baryta.

Prop.—Has a rich red colour; is more stable than the manganic acid, though still very prone to decomposition. Contact with paper or linen as in filtering, particles of cork, organic particles floating in the atmosphere, decompose it rapidly, for which reason Gregory recommends that all solutions containing it should be filtered through a pledget of asbestus, placed in the throat of the funnel. Colouring matters are bleached by it; and in pure water its decomposition begins at 86° and is complete at 212°. On these occasions oxygen gas is abstracted or given out, and hydrated peroxide of manganese subsides. Its salts are more permanent than the free acid, so that most of them may be boiled in solution, especially if concentrated. When heated they give out oxygen gas, and are reconverted into manganates. They deflagrate like nitre with burning charcoal, and detonate powerfully with phosphorus. Their colour in solution is a rich purple, and a small quantity of the salt imparts this colour to a very large quantity of water. When mixed with dilute nitric acid and boiled, oxygen gas is evolved, and hydrated peroxide of manganese subsides, from the respective quantities of which Mitscherlich ascertained the composition of the acid. In addition to the remarkable analogy which its constitution bears to perchloric acid, Mitscherlich finds that permanganate and perchlorate of potassa are isomorphous, an observation confirmed by Miller.

Its eq. is 111·4; symb. $2\ Mn + 7O, \underline{\overset{\cdot\cdot\cdot\cdot\cdot\cdot\cdot}{Mn}}$, or Mn_2O_7.

Protochloride of Manganese.—This compound is best prepared by evaporating a solution of the chloride to dryness by a gentle heat, and heating the residue to redness in a glass tube, while a current of hydrochloric acid gas is transmitted through it. The heat of a spirit-lamp is sufficient for the purpose. It fuses readily at a red heat, and forms a pink-coloured lamellated mass on cooling. It is deliquescent, and of course very soluble in water.

Its eq. is 63·12; symb. $Mn + Cl$, or $MnCl$.

Perchloride of Manganese.—Hist. and Prep.—Dumas discovered this compound, which is readily formed by putting a solution of permanganic into strong sulphuric acid, and then adding fused sea-salt. The hydrochloric and permanganic acids mutually decompose each other; water and perchloride of manganese are generated, and the latter escapes in the form of vapour. The best mode of preparation is to form the green mineral chameleon, and acidulate with sulphuric acid: the solution, when evaporated, leaves a residue of sulphate and permanganate of potassa. This mixture, treated by strong sulphuric acid, yields a solution of permanganic acid, into which are added small fragments of sea-salt, as long as coloured vapour continues to be evolved. (Edin. Journ. of Science, viii. 179.)

Prop.—The perchloride, when first formed, appears as a vapour of a copper or greenish colour; but on traversing a glass tube cooled to −4°, it is condensed into greenish-brown coloured liquid. When generated in a capacious tube, its vapour gradually displaces the air, and soon fills the tube. If it is then poured into a large flask, the sides of which are moist, the colour of the vapour changes instantly on coming into contact with the moisture, a dense smoke of a pretty rose-tint appears, and hydrochloric and permanganic acids are generated. It is hence analogous in composition to permanganic acid, its elements being in such a ratio that

1 eq. Perchloride and 7 eq. Water yield 1 eq. Permang. Acid and 7 eq. Hydrochloric Acid
Mn_2Cl_7 $7\,HO$ Mn_2O_7 $7HCl$.

Hence its eq. is 303·34; symb. $2Mn + 7Cl$, or Mn_2Cl_7.

Perfluoride of Manganese.—This gaseous compound, discovered by Dumas and Wöhler (Edin. Journ. of Science), is best formed by mixing common mineral chameleon with half its weight of fluor-spar, and decomposing the mixture in a platinum vessel by fuming sulphuric acid. The fluoride is then disengaged in the form of a greenish-yellow gas or vapour, of a more intensely yellow tint than chlorine. When mixed with atmospheric air, it instantly acquires a beautiful purple-red colour; and it is freely absorbed by water, yielding a solution of the same red tint. It acts instantly on glass, with formation of fluosilicic acid gas, a brown matter being at the same time deposited, which becomes of a deep purple-red tint on the addition of water.

It may be inferred from the experiments of Wöhler that this yellow gas is a fluoride of manganese; that when mixed with water both compounds are decomposed, and hydrofluoric and permanganic acids generated which are dissolved; that a similar formation of the two acids ensues from the admixture of the yellow gas with atmospheric air, owing to the moisture contained in the latter; and that by contact with glass, fluosilicic acid gas is produced, and anhydrous permanganic acid deposited. In consequence of its acting so powerfully on glass, its other properties have not been ascertained; but from those above mentioned, its composition is obviously similar to that of the the gaseous chloride of manganese.

Its eq. is 186·16; symb. $2Mn + 7F$, or Mn_2F_7.

The *protosulphuret* of *manganese* may be procured by igniting the sulphate with one-sixth of its weight of charcoal in powder. (Berthier.) It is also formed by the action of hydrosulphuric acid gas on the protosulphate at a red heat. (Arfwedson in An. of Phil. vol. vii. N.S.) It occurs native in Cornwall and at Nagyag in Transylvania. It dissolves completely in dilute sulphuric or hydrochloric acid, with disengagement of very pure hydrosulphuric acid gas.

Its eq. is 43·8; symb. $Mn. + S$, or MnS.

SECTION XI.

IRON.

Hist.—Known from the remotest antiquity. The occurrence of native iron, except that of meteoric origin, which always contains nickel and cobalt, is exceedingly rare; and few of the specimens said to be such have been well attested. In combination, however, especially with oxygen and sulphur, it is abundant; being contained in animals and plants, and being diffused so universally in the earth, that there are few mineral substances in which its presence may not be detected. Minerals which contain iron in such form, and in such quantity, as to be employed in the preparation of the metal, are called *ores of iron;* and of these the principal are the following. The red oxides of iron included under the name of red hæmatite; the brown hæmatite of mineralogists, consisting of hydrated peroxide of iron; the black oxide, or magnetic iron ore; and carbonate of protoxide of iron, either pure, or in the form of clay iron ore, when it is mixed with siliceous, calcareous, and other foreign substances. The three former occur most abundantly in primary districts, and supply the finest kinds of iron, as those of Sweden and India; while clay-iron stone, from which most of the English iron is extracted, occurs in secondary deposites, and chiefly in the coal formation.

Prep.—The extraction of iron from its ores is effected by exposing the ore, previously roasted and reduced to a coarse powder, to the action of charcoal, or coke, and lime at a high temperature. The action of carbonaceous matter in depriving the ore of its oxygen is obvious; and the lime plays a part equally important. It acts as a flux by combining with all the impurities of the ore, and forming a fusible compound called a *slag.* The whole mass being thus in a fused state, the particles of reduced metal descend by reason of their greater density, and collect at the bottom; while the slag forms a stratum above, protecting the melted metal from the action of the air. The latter, as it collects, runs out at an aperture in the side of the furnace; and the fused iron is let off by a hole in the bottom, which was previously filled with sand. The process is never successful unless the flux, together with the impurities of the ore, are in such proportion as to constitute a fusible compound. The mode of accomplishing this object is learned only by experience; and as different ores commonly differ in the nature or quantity of their impurities, the workman is obliged to vary his flux according to the composition of the ore with which he operates. Thus if the ore is deficient in siliceous matter, sand must be added; and if it contain a large quantity of lime, proportionally less of that earth will be required. Much is often accomplished by the admixture of different ores with each other. The slag consists of a compound of earthy salts, similar to some siliceous minerals, in which silicic acid is combined with lime, alumina, magnesia, protoxide of manganese, and sometimes oxide of iron. The most usual combination, according to Mitscherlich, is bisilicate of lime and magnesia, sometimes with a little protoxide of iron; a compound which he has obtained in crystals, having the precise form and composition of Augite. Artificial minerals may in fact by such processes be procured, similar in form and composition to those which occur in the earth. We are indebted to Mitscherlich for some valuable facts on this subject. (An. de Ch. et Ph. xxiv. 355.)

The iron obtained by this process is the cast iron of commerce, and contains a considerable quantity of carbon, unreduced ore, and earthy substances. It is converted into soft or malleable iron by exposure to a strong heat while a current of air plays upon its surface. By this means any undecomposed ore is reduced, earthy impurities rise to the surface as slag, and carbonaceous matter is burned. The exposed iron is also more or less oxidized at its surface, and the resulting oxide, being stirred with the fused metal below, facilitates the oxidation of the carbon. As the purity of the iron increases, its fusibility diminishes, until at length, though the temperature continue the same, the iron becomes solid. It is then subjected, while still hot, to the operation of rolling or hammering, by which its particles are approximated, and its tenacity greatly increased. It is then the malleable iron of commerce. It is not, however, absolutely pure; for Berzelius has detected in it about one-half per cent. of carbon, and it likewise contains traces of silicon. The carbonaceous matter may be removed by mixing iron filings with a quarter of its weight of black oxide of iron, and fusing the mixture, confined in a covered hessian crucible, by means of a blast furnace. A little powdered green glass should be laid on the mixture, in order that the iron may be completely protected from the air by a covering of melted glass, and any unreduced oxide dissolved. But the best and readiest mode of procuring iron in a state of perfect purity, is by transmitting hydrogen gas over the pure oxide heated to redness in a tube of porcelain. The oxygen of the oxide unites with hydrogen, and the metal is left in the form of a porous spongy mass.

Prop.—Iron has a peculiar grey colour, and strong metallic lustre, which is susceptible of being heightened by polishing. In ductility and malleability it is inferior to several metals, but exceeds them all in tenacity. At common temperatures it is very hard and unyielding, and its hardness may be increased by being heated and then suddenly cooled; but it is at the same time rendered brittle. When heated to redness it is remarkably soft and pliable, so that it may be beaten into any form, or be intimately incorporated or *welded* with another piece of red-hot iron by hammering. Its texture is fibrous. Its sp. gr. may be estimated at 7·7; but it varies slightly according to the degree with which it has been rolled, hammered, or drawn, and it is increased by fusion. In its pure state it is exceedingly infusible, requiring for fusion the highest temperature of a wind furnace. It is attracted by the magnet, and may itself be rendered permanently magnetic by several processes;—a property of great interest and importance, and which is possessed by no other metal excepting nickel. It retains this quality, however, only within certain temperatures: thus iron of an orange-red heat ceases to be attracted, and a steel magnet loses its polarity at the boiling point of almond oil—a loadstone just below visible ignition. (Faraday.)

Iron, in its ordinary state, has a strong affinity for oxygen. In a perfectly dry atmosphere it undergoes no change; but when moisture is present, its oxidation, or *rusting*, is rapid. In the first part of the change carbonate of protoxide of iron is generated; but the protoxide gradually passes into hydrated peroxide, and the carbonic acid at the same time is evolved. Rust of iron always contains ammonia, a circumstance which indicates that the oxidation is probably accompanied by decomposition of water; and Chevalier has observed that ammonia is also present in the native oxides of iron. Heated to redness in the open air, iron absorbs oxygen rapidly, and is converted into black scales, called the *black oxide* of iron; and in an atmosphere of oxygen gas it burns with vivid scintillations. The same effect was observed by Bierley on exposing a bar of iron at a full white heat to the blast of a powerful pair of bellows. This has been confirmed by D'Arcet, who also obtained the combustion by causing the heated iron to revolve rapidly through the air: for this purpose he attached one extremity of the bar by means of wire to a string, and then whirled it rapidly round. Magnus has observed that the spongy mass obtained by reducing the oxide of iron with hydrogen may be obtained at a heat considerably below that of redness; and that when the iron, thus reduced, is exposed to the air, it takes fire spontaneously, and the oxide is instantly reproduced. This singular property, which Magnus has also remarked in nickel and cobalt prepared in a similar manner, appears to depend on the extremely divided and expanded state of the metallic mass; for when the reduction is effected at a red heat, which enables the metal to acquire its natural degree of compactness, the phenomenon is not observed. If the oxide be mixed with a little alumina, and then reduced at a red heat, the presence of the earth prevents that contraction which would otherwise ensue: the metal is in the same mechanical condition as when it is deoxidized at a low temperature, and its spontaneous combustibility is preserved.

Iron decomposes the vapour of water, by uniting with its oxygen, at all temperatures, from a dull red to a white heat; a singular fact, when it is considered that at the very same temperatures the oxides of iron are reduced to the metallic state by hydrogen gas. (Gay-Lussac in An. de Ch. et de Physique, i. 36.) These opposite effects, various instances of which are known to chemists, are accounted for by the modifications produced in the results of affinity by quantity of matter. Iron is rapidly dissolved by sulphuric and nitric acids: in the former case, hydrogen is disengaged, which is derived according to the commonly received opinion from water, the oxygen of which unites with the metal; but which, on the more modern view, is separated from the sulphuric acid, that acid being considered as a hydrogen acid, $H + SO_4$, and the metal simply taking the place of the hydrogen. In the latter case, the nitric acid itself yields a part of its oxygen. The action of nitric acid on iron is attended by a series of very remarkable phenomena, which have recently been observed by Professor Schonbein. He first observed that nitric acid, of sp. gr. 1·35, though capable of acting with great violence on ordinary iron, was perfectly inert on a portion of iron wire one extremity of which had been made red hot previously to its introduction into the acid. He found, too, that this indifference to nitric acid may be communicated by mere contact from one iron wire to another, by submersion for a few moments into strong nitric acid, or by making it the positive electrode of a galvanic current, the negative electrode having been previously introduced into the acid. It is remarkable that under these circumstances the iron wire possesses the properties of one of gold or platinum, and does not combine with the oxygen liberated at its surface. Faraday, who has examined this voltaic condition of iron with his usual success, has remarked that the same property is communicated to iron by contact with platinum, and that the effect is not limited to nitric acid, but extends to various saline solutions which are usually acted on by iron. For the particulars on this interesting subject the reader may consult the original papers of Schonbein and Faraday in the Phil. Mag. and An. ix. 53; x. 133, 172, 175, 267, 428.

The equivalent of iron has not yet been determined with accuracy. From the analysis of its oxides by Berzelius, Stromeyer, and Gay-Lussac, it may be estimated at 27·16, 27·8, and 28·3. In the uncertainty as to which of these numbers is the most accurate, I shall continue to use 28, the number generally adopted in this country. Its symb. is Fe. The composition of the compounds of iron described in this section is as follows:—

	Iron.				Equiv.	Formulæ.
Protoxide .	28	1 eq.+Oxyg.	8	1 eq.	= 36	$Fe+O$ or FeO.
Peroxide .	56	2 eq.+do.	24	3 eq.	= 80	$2Fe+3O$ or Fe_2O_3.
Ferric Acid .	28	1 eq.+do.	24	3 eq.	= 52	$Fe+3O$ or FeO_3.
Black Oxide		Protoxide	36	1 eq.	=116	$FeO+Fe_2O_3$.
		Peroxide	80	1 eq.		
Protochloride .	28	1 eq.+Chlor.	35·42	1 eq.	= 63·42	$Fe+Cl$ or $FeCl$.
Perchloride .	56	2 eq.+do.	106·26	3 eq.	=162·26	$2F+3Cl$ or Fe_2Cl_3.
Protiodide .	28	1 eq.+Iodine	126·3	1 eq.	=154·3	$Fe+I$ or FeI.
Periodide .	56	2 eq.+do.	378·9	3 eq.	=434·9	$2Fe+3I$ or F_2I_3.
Protobromide .	28	1 eq.+Brom.	78·4	1 eq.	=106·4	$Fe+Br$ or $FeBr$.
Perbromide .	56	2 eq.+do.	235·2	3 eq.	=291·2	$2Fe+3Br$ or Fe_2Br_8.
Protofluoride .	28	1 eq.+Fluor.	18·68	1 eq.	= 46·68	$Fe+F$ or FeF.
Perfluoride .	56	2 eq.+do.	56·04	3 eq.	=112·04	$2Fe+3F$ or Fe_2F_3.
Tetrasulphuret	112	4 eq.+Sulph.	16·1	1 eq.	=128·1	$4Fe+S$ or Fe_4S.
Disulphuret .	56	2 eq.+do.	16·1	1 eq.	= 72·1	$2Fe+S$ or Fe_2S.
Protosulphuret	28	1 eq.+do.	16·1	1 eq.	= 44·1	$Fe+S$ or FeS.
Sesquisulphuret	56	2 eq.+do.	48·3	3 eq.	=104·3	$2Fe+3S$ or Fe_2S_3.
Bisulphuret .	28	1 eq.+do.	32·2	2 eq.	= 60·2	$Fe+2S$ or FeS_2.
Magnetic Pyrites		Bisulph. of Iron	60·2	1 eq.	=280·7	$5FeS+FeS_2$.
		Protosulph. of Iron	220·5	5 eq.		
Diphosphuret .	56	2 eq.+Phosp.	15·7	1 eq.	= 71·7	$2Fe+P$ or Fe_2P.
Perphosphuret	84	3 eq.+do.	62·8	4 eq.	=146·8	$3F+4P$ or Fe_3P_4.
Carburets.	Constitution not determined.					

OXIDES OF IRON.

Protoxide.—This oxide is the base of the native carbonate of iron, and of the green vitriol of commerce. Its existence was inferred some years ago by Gay-Lussac (An. de Ch., vol. lxxx.); but it is doubtful if it has ever been obtained in an insulated form. Its salts, particularly when in solution, absorb oxygen from the atmosphere with such rapidity that they may even be employed in eudiometry. The anhydrous protoxide is believed to be blue, and it sometimes communicates a blue colour to slags containing it. It forms salts which are generally of a bluish-green colour.

Protoxide of iron is precipitated from its salts as a white hydrate by pure alkalies, as a white carbonate by alkaline carbonates, and as a white ferrocyanide by ferrocyanide of potassium. The two former precipitates become first green and then red, and the latter green and blue, by exposure to the air. The solution of gall-nuts produces no change of colour. Hydrosulphuric acid does not act if the protoxide is united with any of the stronger acids; but alkaline hydrosulphates cause a black precipitate, protosulphuret of iron.

Its eq. is 36; symb. $Fe + O, \dot{Fe}$, or FeO.

Peroxide.—Hist. and Prep.—The red or peroxide is a natural product, known to mineralogists under the name of *red hæmatite.* It sometimes occurs massive, at other times fibrous, and occasionally in the form of beautiful rhomboidal crystals. It may be made chemically by dissolving iron in nitra-hydrochloric acid, and adding an alkali. The hydrate of the red oxide of a brownish-red colour subsides, which is identical in composition with the mineral called *brown hæmatite*, and consists of 80 parts or 1 eq. of the peroxide, and 18 parts or 2 eq. of water.

Prop.—Is not attracted by the magnet. Fused with vitreous substances it communicates to them a red or yellow colour. It combines with most of the acids, forming salts, the greater number of which are red or brown. Its presence may be detected by very decisive tests. The pure alkalies, fixed or volatile, precipitate it as the hydrate. Alkaline carbonates have a similar effect, peroxide of iron not forming a permanent salt with carbonic acid. With ferrocyanide of potassium it forms Prussian blue. Sulphocyanide of potassium causes a deep blood-red, and infusion of gall-nuts a black colour. Hydrosulphuric acid converts the peroxide into protoxide of iron, with deposition of sulphur. These reagents, and especially ferrocyanide and sulphocyanide of potassium, afford an unerring test of the presence of minute quantities of peroxide of iron. On this account it is customary, in testing for iron, to convert it into the peroxide, an object which is easily accomplished by boiling the solution with a small quantity of nitric acid.

Its eq. is 80; symb. $2Fe + 3O, \underline{\dddot{Fe}}$, or Fe_2O_3.

Ferric Acid.—The existence of this compound has been established by the researches of Denham Smith and Frémy. It is formed when iron filings are deflagrated with nitre, or when chlorine is passed through a strong solution of potassa or soda in which hydrated peroxide of iron is suspended. In both cases, the ferric acid unites with the alkali, forming a salt of a very deep purple colour. The ferrate of potash is soluble in water, but is precipitated as a dark red, nearly black powder, by a large excess of the alkali; and this powder may be preserved in sealed tubes. The acid is rapidly decomposed when separated from its salts, yielding oxygen and peroxide. It corresponds in composition to manganic acid.

Its eq. is 52; symb. $Fe + 3O$, or FeO_3.

Black or Magnetic Oxide.—Hist. and Prep.—This substance, the *oxidum ferroso-ferricum* of Berzelius, long supposed to be protoxide of iron, contains more oxygen than the protoxide, and less than the red oxide. It cannot be regarded as a definite compound of iron and oxygen; but it is composed of the two real oxides. It occurs native, frequently crystallized in the form of a regular octohedron and dodecahedron; and it is not only attracted by the magnet, but is itself sometimes magnetic. It is always formed when iron is heated to redness in the open air; and is likewise generated by the contact of watery vapour with iron at elevated temperatures. The composition of the product, however, varies with the duration of the process and the temperature which is employed. Thus, according to Bucholz, Berzelius, and Thomson, 100 parts of iron, when oxidized by steam, unite with nearly 30 of oxygen; whereas in a similar experiment performed by Gay-Lussac, 37·8 parts of oxygen were absorbed. The oxide of Gay-Lussac has the composition stated in the table; and Berzelius thinks that of magnetic iron ore to be similar. This has been satisfactorily confirmed by Abich, by precipitating a mixture of the two oxides from their solution in sulphuric acid, in which they were contained in their equivalent proportions. The green precipitate which falls he found to be as highly magnetic as the native magnetic iron ore, and to suffer no change on exposure to the atmosphere. But if the protoxide were contained in the solution in greater quantity, its presence in the precipitate as such was indicated by the production of the hydrated peroxide on exposure to the air. An excess of the peroxide diminished the magnetic effects. (An. de Ch. et Ph., lx. 369.) Gregory has observed, that when a solution of protosulphate of iron is divided into two equal parts, one of which is peroxidized, then mixed with the other, and precipitated by ammonia at a boiling heat, a second black oxide is obtained, which does not attract oxygen in drying, and is highly magnetic. Its composition must be $2FeO + Fe_2O_3$; as the two solutions contain equal quantities of iron; and Gregory suggests that it may occur native as a variety of magnetic iron ore. Wöhler (Liebig's Annalen, xxii. 56,) erroneously gives the above proportions for forming the common magnetic oxide, $FeO, + Fe_2O_3$; to obtain which 1 part of protosulphate should be mixed with 2 of the same salt peroxidized by nitric acid. M. Mosander states, that on heating a bar of iron in the open air, the outer layer of the scales contains a greater quantity of peroxide than the inner layer. The former consists of 1 eq. of peroxide to 4 of the protoxide, and in the latter are contained 1 eq. of peroxide to 6 eq. of protoxide. The inner layer seems uniform in composition; but the outer is variable, its more exposed parts being richer in oxygen.

The nature of the black oxide is farther elucidated by the action of acids. On digesting the black oxide in sulphuric acid, an olive-coloured solution is formed, containing two salts, sulphate of the peroxide and protoxide, which may be separated from each other by means of alcohol. (Proust and Gay-Lussac.) The solution of these mixed salts gives green precipitates with alkalies, and a very deep blue ink with infusion of gall-nuts. The black oxide of iron is the cause of the dull green colour of bottle glass.

Its eq. is 116: symb. $FeO + Fe_2O_3$.

Protochloride of Iron.—Prep.—This compound is formed by transmitting dry hydrochloric acid gas over iron at a red heat, when hydrogen gas is evolved, and the surface of the iron is covered with a white crystalline protochloride, which at a stronger heat is sublimed. Also, on acting with hydrochloric acid on iron, which is dissolved with evolution of hydrogen gas, evaporating to dryness, and heating to redness in a tube without exposure to the air, a grey crystalline protochloride is left; but it contains some protoxide formed by an interchange of elements between the last portions of water and the chloride, hydrochloric acid being also generated.

Prop.—It dissolves freely in water, yielding a pale green solution, from which rhomboidal prisms of the same colour are obtained by evaporation. The crystals contain several equivalents of water of crystallization, deliquesce by exposure to the air, owing to the formation of perchloride, and are soluble in alcohol as well as water. The aqueous solution absorbs oxygen from the air, and becomes yellow from the formation of perchloride of iron: one portion of iron takes oxygen from the air, and yields its chlorine to another portion of iron, whereby perchloride and peroxide of iron are generated, and the latter falls as an ochreous sediment combined with some of the perchloride. A solution of the protochloride of iron dissolves binoxide of nitrogen with the same phenomena as the protosulphate, a circumstance favourable to the view entertained by many that protochloride of iron is converted by water into hydrochlorate of the protoxide.

Its eq. is 63·42; symb. $Fe + Cl$, or $FeCl$.

Perchloride of Iron.—It is formed by the combustion of iron wire in dry chlorine gas, and by transmitting that gas over iron moderately heated, when it is obtained in small iridescent plates of a red colour, which are volatile at a heat a little above 212°, deliquesce readily, and dissolve in water, alcohol, and ether. On agitating ether with a strong aqueous solution of the perchloride, the ether abstracts a part of it, and acquires a gold-yellow colour. The readiest mode of obtaining a solution of the perchloride is to dissolve peroxide of iron in hydrochloric acid. On concentrating to the consistence of syrup and cooling, it separates as red crystals, which by distillation yield at first water and hydrochloric acid, and then anhydrous perchloride of iron, leaving a compound of peroxide and perchloride of iron in crystalline laminæ. The formation of peroxide appears due to an interchange of elements between it and water. The same kind of interchange ensues between the vapours of water and the perchloride at a high temperature; and this is probably the source, as Mitscherlich suggests, of the crystals of peroxide of iron found in volcanic products.

Its eq. is 162·26; symb. $2Fe + 3Cl$, or Fe_2Cl_3.

Protiodide of Iron.—It exists as a pale green solution when iodine is digested with water and iron wire, the latter being in excess; and on evaporating the solution, without exposure to the air, to dryness and heating moderately, the protiodide is fused, and on cooling becomes an opaque crystalline mass of an iron-grey colour and metallic lustre. It is deliquescent and very soluble in water and alcohol. Its aqueous solution attracts oxygen rapidly from the air, undergoing the same kind of change as the protochloride: to preserve a solution of protiodide as such a long piece of iron wire should be kept permanently in the liquid. This compound has been very successfully employed in medical practice by my colleague Dr. A. T. Thomson.

Its eq. is 154·3; symb. $Fe + I$, or FeI.

The *periodide*, of a yellow or orange colour according to the strength of the solution, is obtained by freely exposing a solution of the protiodide to the air, or digesting iron wire with excess of iodine, gently evaporating, and subliming the periodide. It is a volatile red compound, deliquescent, and soluble in water and alcohol.

Its eq. is 434·9; symb. $2Fe + 3I$, or Fe_2I_3.

The *bromides* of iron are formed under similar conditions to the chlorides and iodides, and are very analogous to them in their properties.

Protofluoride of Iron is best prepared by dissolving iron in a solution of hydrofluoric acid, out of which it crystallizes as the acid becomes saturated, in small white square tables, which are sparingly soluble in water, and become pale yellow by the action of the air. By heat they part with their water of crystallization, and afterwards bear a red heat without decomposition. (Berzelius.)

Its eq. is 46·68; symb. $Fe + F$, or FeF.

The *perfluoride* is formed by dissolving peroxide of iron in hydrofluoric acid, and yields a colourless solution even when saturated. By evaporation it is left as a crystalline mass of a pale flesh-colour, and of a mild astringent taste. It is sparingly soluble in water.

Its eq. is 112·04; symb. $2Fe + 3F$, or Fe_2F_3.

Sulphurets of Iron.—These elements have for each other a remarkably strong affinity, and unite under various circumstances and in several proportions. The two lowest degrees of sulphuration, the *tetrasulphuret* and *disulphuret*, were prepared by Arfwedson by transmitting a current of hydrogen gas at a red heat over the anhydrous disulphate of peroxide of iron to procure the tetrasulphuret, and over anhydrous sulphate of protoxide of iron for the disulphuret. In both cases sulphurous acid and water are evolved, and the resulting sulphurets are left as greyish black powders susceptible of a metallic lustre by friction. They both dissolve in dilute sulphuric acid with evolution of hydrogen and hydrosulphuric acid gases.

Protosulphuret of Iron is prepared by heating thin laminæ of iron to redness with sulphur in a covered hessian crucible, and continuing the heat until any excess of sulphur is expelled. The iron is found with a crust of protosulphuret, which is brittle, of a yellowish-grey colour and metallic lustre, and is attracted by the magnet. When pure it is completely dissolved by dilute sulphuric acid, yielding pure hydrosulphuric acid. The protosulphuret of iron exists in nature as an ingredient in variegated copper pyrites; and it falls on mixing hydrosulphate of ammonia with sulphate of protoxide of iron as a black precipitate, which oxidizes rapidly by absorbing oxygen from the air as soon as the excess of hydrosulphate of ammonia is removed by washing.

Its eq. is 44·1; symb. $Fe + S$, or FeS.

The *sesquisulphuret* is formed in the moist way by adding perchloride of iron drop by drop to hydrosulphate of ammonia or sulphuret of potassium in excess, and falls as a black precipitate, which is oxidized readily by the air. In the dry way it is slowly produced by the action of hydrosulphuric acid gas on peroxide of iron at a heat not exceeding 212°, water being also formed; and by the action of the same gas on the hydrated peroxide at common temperatures. This sulphuret, when anhydrous, has a yellowish-grey colour, is not attracted by the magnet, and dissolves in dilute sulphuric or hydrochloric acid, yielding hydrosulphuric acid and a residue of bisulphuret of iron. (Berzelius.)

Its eq. is 104·3; symb. $2Fe + 3S$, or Fe_2S_3.

Bisulphuret of iron, iron pyrites of mineralogists, exists abundantly in the earth. It occurs in cubes or some allied form, has a yellow colour, metallic lustre, a density of 4·981, and is so hard that it strikes fire with steel. Some varieties have a white colour; but these usually contain arsenic. Others occur in rounded nodules, have a radiated structure divergent from a common centre, are often found in beds of clay, and are much disposed by the influence of air and moisture to yield sulphate of oxide of iron: these are suspected by Berzelius to be compounds of protosulphuret and bisulphuret of iron.

Bisulphuret of iron is not attacked by any of the acids except the nitric, and its best solvent is the nitro-hydrochloric acid. Heated in close vessels it gives off nearly half its sulphur, and is converted into magnetic iron pyrites. By heat and air together it yields peroxide of iron. Its eq. is 60·2; symb. $Fe + 2S$, or FeS_2.

Magnetic iron pyrites.—This is a natural product, termed magnetic pyrites, from being attracted by the magnet, and was formerly regarded as protosulphuret of iron; but Stromeyer has shown that its elements are in such a ratio, that it may be regarded as a compound of bisulphuret and protosulphuret. It is formed by heating the bisulphuret to redness in close vessels, by fusing iron filings with half their weight of sulphur, or by rubbing sulphur upon a rod of iron heated to whiteness. It is soluble in dilute sulphuric acid, yielding hydrosulphuric acid gas and a residue of sulphur. It is much more oxidable by air and moisture than the pure bisulphuret. Its eq. is 280·7; symb. $5FeS + FeS_2$.

Diphosphuret of Iron.—It is prepared by exposing the phosphate of protoxide of iron to a strong heat in a covered crucible lined with charcoal, the excess of phosphorus being dissipated in vapour. It is a fused granular mass, of the colour and lustre of iron, but very brittle, and is not attacked by hydrochloric acid. It is sometimes contained in metallic iron, to the properties of which it is very injurious by rendering it brittle at common temperatures. Its eq. is 71·7; symb. $2Fe + P$, or Fe_2P.

The *perphosphuret* has been obtained by Rose by the action of phosphuretted hydrogen gas on sulphuret of iron at a moderate temperature, and resembles the former in its properties.

Its eq. is 146·8; symb. $3Fe + 4P$, or Fe_3P_4.

Carburets of Iron.—Carbon and iron unite in very various proportions; but there are three compounds very distinct from each other—namely, graphite, cast or pig iron, and steel.

Graphite, also known under the names of *plumbago* and *black lead*, occurs not unfrequently as a mineral production, and is found in great purity at Borrowdale in Cumberland. It may be made artificially by exposing iron with excess of charcoal to a violent and long-continued heat; and it is commonly generated in small quantity during the preparation of cast iron. Pure specimens contain about four or five per cent. of iron, but sometimes its quantity amounts to 10 per cent. Most chemists believe the iron to be chemically united with the charcoal; but according to the researches of Karsten of Berlin, native graphite is only a mechanical mixture of charcoal and iron, and is not unfrequently pure carbon, while artificial graphite is a real carburet.

Graphite is exceedingly unchangeable in the air, and, like charcoal, is attacked with difficulty by chemical reagents. It may be heated to any extent in close vessels without change; but if exposed at the same time to the air, its carbon is entirely consumed, and oxide of iron remains. It has an iron grey colour, metallic lustre, and granular texture; and it is soft and unctuous to the touch. Its chief use is in the manufacture of pencils and crucibles, and in burnishing iron to protect it from rust.

Cast iron is the product of the process for extracting iron from its ores, and is commonly regarded as a real compound of iron and charcoal. It always contains impurities, such as charcoal, undecomposed ore, and earthy matters, which are often visible by mere inspection; and sometimes traces of chromium, manganese, sulphur, phosphorus, and arsenic are present. It fuses readily at 278·6° (Daniell), which is a full red heat, and in cooling it acquires a crystalline granular texture. The quality of different specimens is by no means uniform; and two kinds, white and grey cast iron, are in particular distinguished from each other. The former is exceedingly hard and brittle, sometimes breaking like glass from sudden change of temperature; while the latter is softer and much more tenacious. This difference appears owing to the mode of combination, rather than to a difference in the proportion of carbon; for the white variety may be converted into the grey by exposure to a strong heat and cooling slowly, and the grey may be changed into the white by being heated and rapidly cooled. According to Karsten the carbon of the latter is combined with the whole mass of iron, and amounts as a maximum to 5·25 per cent.; but in some specimens its proportion is considerably less. The former, on the contrary, contains from 3·15 to 4·65 per cent. of carbon, of which about three-fourths are in the state of graphite, and are left as such after the iron is dissolved by acids; while the remaining fourth is in combination with the whole mass of metal, constituting a carburet which is very similar to steel. Grey cast iron may hence be regarded as a kind of steel, in which graphite is mechanically mixed.

Steel is commonly prepared in this country by the process of cementation, which consists in filling a large furnace with alternate strata of bars of the purest malleable iron and powdered charcoal, closing every aperture so as perfectly to exclude atmospheric air, and keeping the whole during several days at a red heat. By this treatment the iron gradually combines with from 1·3 to 1·75 per cent. of carbon, its texture is greatly changed, and its surface is blistered. It is subsequently hammered at a red heat into small bars, and may be welded either with other bars of steel or with malleable iron. Mackintosh, of Glasgow, has introduced an elegant process of forming steel by exposing heated iron to a current of coal gas, when carburetted hydrogen is decomposed, its carbon enters into combination with iron, and hydrogen gas is evolved.

In ductility and malleability it is far inferior to iron; but exceeds it greatly in hardness, sonorousness, and elasticity. Its texture is also more compact, and it is susceptible of a higher polish. It sustains a full red heat without fusing, and is therefore less fusible than cast iron; but it is much more so than malleable iron. By fusion it forms cast steel, which is more uniform in composition and texture, and possesses a closer grain, than ordinary steel.

SECTION XII.

ZINC.—CADMIUM.

ZINC.

Hist and Prep.—This metal was first mentioned under the term *zinetum* in the sixteenth century by Paracelsus; but it was probably known at a much earlier period. In commerce, it is often called *spelter*, and is obtained either from *calamine*, native carbonate of zinc, or from the native sulphuret, *zinc blende* of mineralogists. It is procured from the former by heat and carbonaceous matters; and from the latter by a similar process after the ore has been previously oxidized by *roasting*, that is, by exposure to the air at a low red heat. Its preparation affords an instance of what is called *distillation by descent*. The furnace or crucible for reducing the ore is closed above, and in its bottom is fixed an iron tube, the upper aperture of which is in the interior of the crucible, and its lower terminates just above a vessel of water. The vapour of zinc, together with all the gaseous products, passes through this tube, and the zinc is condensed. The first portions are commonly very impure, containing cadmium and arsenic, the period of their disengagement being indicated by what the workmen call the *brown blaze;* but when the *blue blaze* begins, that is, when the metallic vapour burns with a bluish white flame, the zinc is collected. As thus obtained, it is never quite pure: it frequently contains traces of charcoal, sulphur, cadmium, arsenic, lead, and copper; and iron is always present. It may be freed from these impurities by distillation,—by exposing it to a white heat in an earthern retort, to which a receiver full of water is adapted; but the first portions, as liable to contain arsenic and cadmium, should be rejected.

Prop.—It has a strong metallic lustre, and a bluish white colour. Its texture is lamellated, and its sp. gr. about 7. It is a hard metal, being acted on by the file with difficulty. At low or high degrees of heat it is brittle; but at temperatures between 210° and 300°, it is both malleable and ductile, a property which enables zinc to be rolled or hammered into sheets of considerable thinness. Its malleability is considerably diminished by the impurities which the zinc of commerce contains. It fuses at 773° (Daniell), and when slowly cooled crystallizes in four or six-sided prisms. Exposed in close vessels to a white heat, it sublimes unchanged.

Zinc undergoes little change by the action of air and moisture. When fused in open vessels it absorbs oxygen, and forms the white oxide, called flowers of zinc. Heated to full redness in a covered crucible, it bursts into flame as soon as the cover is removed, and burns with a brilliant white light. The combustion ensues with such violence, that the oxide as it is formed is mechanically carried up into the air. The heat at which it begins to burn is estimated by Daniell at 941° F. Zinc is readily oxidized by dilute sulphuric or hydrochloric acid, and the hydrogen which is evolved contains a small quantity of metallic zinc in combination.

Gay-Lussac and Berzelius found that the protoxide of zinc consists of 100 parts of metallic zinc and 24·8 of oxygen, being a ratio of 32·3 to 8. Its other combinations justify the adoption of 32·3 as the eq. of zinc; its symb. is Zn. The composition of its compounds described in this section is as follows:—

	Zinc.			Equiv.	Formulæ.
Protoxide .	32·3	1 eq.+Oxygen	8	1 eq.= 40·3	$Zn+O$ or ZnO.
Peroxide .	Composition uncertain.				
Chloride .	32·3	1 eq.+Chlorine	35·42	1 eq.= 67·72	$Zn+Cl$ or $ZnCl$.
Iodide .	32·3	1 eq.+Iodine	126·3	1 eq.=158·6	$Zn+I$ or ZnI.
Bromide .	32·3	1 eq.+Bromine	78·4	1 eq.=110·7	$Zn+Br$ or $ZnBr$.
Fluoride .	32·3	1 eq.+Fluorine	18·68	1 eq.= 50·98	$Zn+F$ or ZnF.
Sulphuret .	32·3	1 eq.+Sulphur	16·1	1 eq.= 48·4	$Zn+S$ or ZnS.

Protoxide of Zinc.—This is the only oxide of zinc which acts as a salifiable base, and the only one of known composition. It is generated during the solution of zinc in dilute sulphuric acid, and may be obtained in a dry state by collecting the flakes which rise during the combustion of zinc, or by heating the carbonate to redness. At common temperatures it is white; but when heated to low redness, it assumes a yellow colour, which gradually disappears on cooling. It is quite fixed in the fire. It is insoluble in water, and therefore does not affect the blue colour of plants; but it is a strong salifiable base, forming regular salts with acids, most of which are colourless. It combines also with some of the alkalies.

The presence of zinc is easily recognized by the following characters:—The oxide is precipitated from its solutions as a white hydrate by pure potassa or ammonia, and as carbonate by carbonate of ammonia, but is completely redissolved by an excess of the precipitant. The fixed alkaline carbonates precipitate as permanently as white carbonate of oxide of zinc. Hydrosulphate of ammonia causes a white precipitate, a hydrated sulphuret of zinc. Hydrosulphuric acid acts in a similar manner, if the solution is quite neutral; but it has no effect if an excess of any strong acid is present.

Its eq. is 40·3; symb. $Zn + O$, $\ddot{Z}n$, or ZnO.

When metallic zinc is exposed for some time to air and moisture, or is kept under water, it acquires a superficial coating of a grey matter, which Berzelius describes as a sub-oxide. It is probably a mixture of metallic zinc and the white oxide, into which it is resolved by the action of acids. The peroxide is prepared, according to Thenard, by acting on hydrated white oxide of zinc with peroxide of hydrogen diluted with water. It resolves itself so readily into oxygen and the oxide already described, that it cannot be preserved even under the surface of water; and its composition is quite unknown.

Chloride of Zinc.—This compound is formed, with evolution of heat and light, when zinc filings are introduced into chlorine gas; and it is readily prepared by dissolving zinc in hydrochloric acid, evaporating to dryness, and heating the residue in a tube through which dry hydrochloric acid gas is transmitted. It is colourless, fusible at a heat a little above 212°, has a soft consistence at common temperatures, hence called *butter of zinc*, sublimes at a red heat, and deliquesces in the air.

Its eq. is 67·72; symb. $Zn + Cl$, or $ZnCl$.

Iodide of Zinc is prepared by digesting iodine in water with zinc filings in excess. A colourless solution results, which by evaporation yields a deliquescent iodide. It is used in medicine. By heat in close vessels it may be sublimed, and then crystallizes in brilliant needles; but if heated in the open air, oxide of zinc is formed, and iodine expelled. If zinc is digested in water with an excess of iodine, a brown solution results, which probably contains a biniodide.

Its eq. is 158·6; symb. $Zn + I$, or ZnI.

Bromide of Zinc may be formed by a process similar to that for the iodide, but its properties have not been studied.

Its eq. is 110·7; symb. $Zn + Br$, or $ZnBr$.

Fluoride of Zinc is obtained by acting directly on oxide of zinc with hydrofluoric acid, and is a white compound of sparing solubility.

Its eq. is 50·98; symb. $Zn + F$, or ZnF.

Sulphuret of Zinc.—This compound is well known to mineralogists under the name of *zinc blende*, and occurs in dodecahedral crystals or some allied form. Its structure is lamellated, lustre adamantine, and colour variable, being sometimes yellow, red, brown, or black. It may be formed artificially by igniting in a closed crucible a mixture of oxide of zinc and sulphur, or sulphate of oxide of zinc and charcoal, or by drying the hydrated sulphuret of zinc. Its eq. is 48·4; symb. $Zn + S$, or ZnS.

CADMIUM.

Hist.—Cadmium, so called (from *καδμεια*, a term applied to calamine and to the volatile matters which rise from the furnace in preparing brass) because it is associated with zinc, was discovered in the year 1817, by Stromeyer, in an oxide of zinc which had been prepared for medical use; and he has since found it in several of the ores of that metal, especially in a radiated blende from Bohemia, which contains about five per cent. of cadmium. The late Dr. Clarke detected its existence in some of the zinc ores of Derbyshire, and in the common zinc of commerce. The mineral Greenockite, which occurs along with prehnite and zeolites, in the trap rocks of Renfrewshire, in the form of fine yellow crystals, has been shown by Connell to be pure sulphuret of cadmium. Herapath has found it in considerable quantitity in the zinc works near Bristol. During the reduction of calamine by coal, the cadmium, which is very volatile, flies off in vapour mixed with soot and some oxide of zinc, and collects in the roof of the vault, just above the tube leading from the crucible. Some portions of this substance yielded from 12 to 20 per cent. of cadmium. (An. of Phil. xiv. and xvii.)

Prep.—The process by which Stromeyer separates cadmium from zinc or other metals is the following. The ore of cadmium is dissolved in dilute sulphuric or hydrochloric acid, and after adding a portion of free acid, a current of hydrosulphuric acid gas is transmitted through the liquid, by which means the cadmium is precipitated as sulphuret, while the zinc continues in solution. The sulphuret of cadmium is then decomposed by nitric acid, and the solution evaporated to dryness. The dry nitrate is dissolved in water, and an excess of carbonate of ammonia added. The white carbonate of oxide of cadmium subsides, which, when heated to redness, yields a pure oxide. By mixing this oxide with charcoal, and exposing the mixture to a red heat, metallic cadium is sublimed.

A very elegant process for separating zinc from cadmium was proposed by Wollaston. The solution of the mixed metals is put into a platinum capsule, and a piece of metallic zinc is placed in it. If cadmium is present, it is reduced, and adheres so tenaciously to the capsule, that it may be washed with water without danger of being lost. It may then be dissolved either by nitric or dilute hydrochloric acid.

Prop.—Cadmium, in colour and lustre, has a strong resemblance to tin, but is somewhat harder and more tenacious. It is very ductile and malleable. Its sp. gr. is 8·604 before being hammered, and 8·694 afterwards. It melts at about the same temperature as tin, and is nearly as volatile as mercury, condensing like it into globules which have a metallic lustre. Its vapour has no odour. When heated in the open air, it absorbs oxygen, and is converted into an oxide. Cadmium is readily oxidized and dissolved by nitric acid, which is its proper solvent. Sulphuric and hydrochloric acids act upon it less easily, and the oxygen is then derived from water.

The eq. of cadmium, deduced from Stromeyer's analysis of its oxide, is 55·8. Its symb. is Cd. The composition of its compounds described in this section as follows:—

	Cadmium.			Equiv.	Formulæ.
Oxide of Cadm.	55·8	1 eq.+Oxygen	8	1 eq.= 63·8	$\mathrm{Cd+O}$ or CdO.
Chloride . .	55·8	1 eq.+Chlorine	35·42	1 eq.= 91·22	$\mathrm{Cd+Cl}$ or CdCl.
Iodide . .	55·8	1 eq.+Iodine	126·3	1 eq.=182·1	$\mathrm{Cd+I}$ or CdI.
Sulphuret .	55·8	1 eq.+Sulphur	16·1	1 eq.= 71·9	$\mathrm{Cd+S}$ or CdS.

Oxide of Cadmium.—This, the only known oxide of Cadmium, is prepared by igniting its carbonate, has an orange colour, is fixed in the fire, and is insoluble in water. It has no action on test paper, but is a strong alkaline base, forming neutral salts with acids. It is precipitated as a white hydrate by pure ammonia, but is redissolved by excess of that alkali. It is precipitated permanently by pure potassa or soda as a hydrate, and by all the alkaline carbonates as carbonate of oxide of cadmium.

Its eq. is 63·8; symb. $\mathrm{Cd + O}$, Cd, or CdO.

Chloride of Cadmium.—By dissolving oxide of cadmium in hydrochloric acid and concentrating duly, the chloride with water of crystallization crystallizes in transparent four-sided rectangular prisms, which lose their water by heat and even in a dry air, fuse at a heat short of redness, and acquire a lamellated texture in cooling. At a high temperature it is sublimed.

Its eq. is 91·22; symb. $Cd + Cl$, or $CdCl$.

Iodide of Cadmium may be formed in the same manner as iodide of zinc, is soluble in water and alcohol, and crystallizes by evaporation in large, colourless, transparent, hexagonal tables, which do not change in the air, and have a pearly lustre. By heat they lose water, and then fuse. Its eq. is 182·1; symb. $Cd + I$, or CdI.

Sulphuret of Cadmium occurs pure and crystallized in the mineral Greenockite, and in mixture or combination in some kinds of zinc blende, and is easily prepared by the action of hydrosulphuric acid on a salt of cadmium. It has a yellowish-orange colour, and is distinguished from the sulphurets of arsenic by being insoluble in pure potassa, and by sustaining a white heat without subliming. (Stromeyer.)

Its eq. is 71·9; symb. $Cd + S$, or CdS.

SECTION XIII.

TIN.

Hist. and Prep.—Was known to the ancients, who obtained it principally, if not solely, from Cornwall. The tin of commerce is distinguished in two varieties, called *block* and *grain tin*, both of which are procured from the native oxide by means of heat and charcoal. In Cornwall, which has been celebrated for its tin-mines during many centuries, the ore is both extracted from veins and found in the form of rounded grains among beds of rolled materials, which have been deposited by the action of water. These grains, commonly called *stream tin*, contain a very pure oxide, and yield the purest kind of grain tin. An inferior sort is prepared by heating bars of tin, extracted from the common ore, to very near their point of fusion, when the more fusible parts, which are the purest, flow out; and the less fusible portions constitute block tin. The usual impurities are iron, copper, and arsenic.

Prop.—It has a white colour, and a lustre resembling that of silver. The brilliancy of its surface is but very slowly impaired by exposure to the atmosphere, nor is it oxidized even by the combined agency of air and moisture. Its malleability is very considerable, for the thickness of common tin-foil does not exceed 1-1000th of an inch. In ductility and tenacity it is inferior to several metals. It is soft and inelastic, and when bent backwards and forwards emits a peculiar crackling noise. Its sp. gr. is about 7·291. At 442° it fuses, and if exposed at the same time to the air, its surface tarnishes, and a grey powder is formed. When heated to whiteness, it takes fire and burns with a white flame, being converted into peroxide of tin.

The eq. of tin deduced by Berzelius from his analysis of its oxides is 57·9; its symb. is Sn. The composition of the compounds of tin described in this section is as follows:—

	Tin.			Equiv.	Formulæ.
Protoxide	57·9	1 eq.+Oxygen	8	1 eq.= 65·9	$Sn+O$ or SnO.
Sesquioxide	105·8	2 eq.+ . .	24	3 eq.=129·8	$2Sn+3O$ or Sn_2O_3.
Binoxide	57·9	1 eq.+ . .	16	2 eq.= 73·9	$Sn+2O$ or SnO_2.
Protochloride	57·9	1 eq.+Chlorine	35·42	1 eq.= 93·32	$Sn+Cl$ or $SnCl$.
Bichloride	57·9	1 eq.+ . .	70·84	2 eq.=128·74	$Sn+2Cl$ or $SnCl_2$.
Protiodide	57·9	1 eq.+Iodine	126·3	1 eq.=184·2	$Sn+I$ or SnI.
Biniodide	57·9	1 eq.+ . .	252·6	2 eq.=310·5	$Sn+2I$ or SnI_2.
Protosulphuret	57·9	1 eq.+Sulphur	16·1	1 eq.= 74·0	$Sn+S$ or SnS.
Sesquisulph.	115·8	2 eq.+ . .	48·3	3 eq.=164·1	$2Sn+3S$ or Sn_2S_3.
Bisulphuret	57·9	1 eq.+ . .	32·2	2 eq.= 90·1	$Sn+2S$ or SnS_2.
Terphosphuret	57·9	1 eq.+Phosph.	47·1	3 eq.=105·0	$Sn+3P$ or SnP_3.

Protoxide of Tin.—Prep.—When chloride of tin in solution is mixed with an alkaline carbonate, hydrated oxide of tin falls, which may be obtained as such in a dry form by washing with warm water, and drying at a heat not above 196°, with the least possible exposure to the air. The best mode of obtaining the anhydrous oxide is by heating the hydrate to redness in a tube from which air is excluded by a current of carbonic acid gas. The same oxide is formed when tin is kept for some time fused in an open vessel.

Prop.—Its sp. gr. is 6·666. At common temperatures it is permanent in the air; but if touched by a red-hot body it takes fire, and is converted into the peroxide. It is dissolved by the sulphuric and hydrochloric acids, as also by dilute nitric acid; and the pure fixed alkalies likewise dissolve it. From the alkaline solution metallic tin is gradually deposited, and peroxide of tin remains in solution. Its salts are remarkably prone to absorb oxygen, both from the air and from compounds which yield oxygen readily. Thus it converts peroxide of iron into protoxide, and throws down mercury, silver, and platinum in the metallic state from their salts. With a solution of gold it causes a purple precipitate, the *purple of Cassius*, which appears to be a compound of peroxide of tin and protoxide of gold. By this character protoxide of tin is recognized with certainty. It is thrown down by hydrosulphuric acid as black protosulphuret of tin.

Its eq. is 65·9; symb. $Sn + O$, $\dot{Sn}$, or SnO.

Sesiquioxide of Tin.—Fuchs has lately succeeded in preparing this oxide by mixing recently precipitated and moist hydrated peroxide of iron with a solution of protochloride of tin, as free as possible from hydrochloric acid; when, by an interchange of elements,

1 eq. Perox. Iron and	2 eq. Chloride of Tin	yield	1 eq. Sesquiox. Tin and	2 eq. Chlo. Iron
Fe_2O_3	2SnCl		Sn_2O_3	2FeCl.

The sesquioxide falls as a slimy grey matter, and in general rather yellow from adhering oxide of iron. Berzelius obtained it purer by using a solution made by saturating hydrochloric acid as far as possible with hydrated peroxide of iron. The sesquioxide of tin, while moist, is soluble in hydrochloric acid, and the solution strikes the purple of Cassius with gold; and it is readily soluble in a solution of ammonia, which distinguishes it from the protoxide of tin, just as its action on gold does from the binoxide. (Pog. Annalen, xxviii. 443.)

Its eq. is 129·8; symb. $2Sn + 3O$, $\underline{\overset{\cdots}{Sn}}$, or Sn_2O_3.

Peroxide of Tin.—*Prep.*—Most conveniently by the action of nitric acid on metallic tin. The acid in its most concentrated state does not act easily upon tin; but when a small quantity of water is added, violent effervescence takes place, owing to the evolution of nitrous acid and binoxide of nitrogen, and a white powder, the hydrated peroxide, is produced. On edulcorating this substance, and heating it to redness, watery vapour is expelled, and the pure peroxide, of a straw-yellow colour, remains. In this process ammonia is generated, a circumstance which proves water as well as nitric acid to be decomposed. Peroxide of tin may likewise be obtained by precipitation from a solution of perchloride of tin by potassa, ammonia, or the alkaline carbonates; but in this case it falls a very bulky hydrate, different from the other hydrate both in appearance and several of its chemical properties. Thus, the latter dissolves readily in sulphuric, nitric, and hydrochloric acid, even when diluted; while the former is completely insoluble in the same acids, even when concentrated. It unites, indeed, with hydrochloric acid, and the compound is soluble in pure water.

Prop.—It has very little disposition in any state to unite with acids, and when dissolved by them, is very apt to separate itself spontaneously as a gelatinous hydrate. It acts the part of a feeble acid: it reddens litmus when its hydrate moistened is laid upon it, and it unites with the pure alkalies, forming soluble compounds which are called *stannates.*

Peroxide of tin is recognized by its insolubility in acids in its anhydrous state; by separating from its solution by means of hydrochloric acid as a bulky hydrate by any of the alkalies or alkaline carbonates, which is easily and completely dissolved by pure potassa or soda in excess; and by yielding with hydrosulphuric acid the yellow bisulphuret of tin, which is also soluble in pure potassa. Peroxide of tin, when melted with glass, forms a white enamel.

Its eq. is 73·9; symb. $Sn + 2O$, $\ddot{Sn}$, or SO_2.

Protochloride of Tin.—This compound is obtained by transmitting hydrochloric acid gas over metallic tin heated in a glass tube, when hydrogen gas is evolved; or by distilling a mixture either of granulated tin with an equal weight of bichloride of mercury, or of an amalgam of tin with calomel, urging the heat till the mercury is expelled. In this state it is a grey solid, of a resinous lustre, which fuses below redness, and at a higher temperature sublimes. It is obtained by crystallization from a concentrated solution of the chloride in crystals, which are sometimes in small white needles, and at others in large transparent prisms, and consist of 93·32 parts or 1 eq. of protochloride of tin, and 27 parts or 3 eq. of water. On heating these crystals, they not only lose water, but reaction ensues between the elements of water and the chloride, hydrochloric acid gas is evolved, and protoxide of tin remains combined with the chloride. The same kind of compound is formed when a large quantity of the water is poured upon the crystals; the solution contains protochloride of tin and hydrochloric acid, and a white powder subsides which consists of 1 eq. of the protochloride, 1 eq. of protoxide, and 2 eqs. of water. (Berzelius.)

A solution of protochloride of tin is obtained by heating granulated tin in strong hydrochloric acid as long as hydrogen gas continues to be evolved. This solution is much employed as a deoxidizing agent, being more powerful than the sulphate or nitrate of the protoxide; owing apparently to the tendency of the protochloride of tin to resolve itself into bichloride and metallic tin, the latter taking oxygen or chlorine from any metallic solutions which yield them readily. Its eq. is 93·32; symb. $Sn + Cl$, or $SnCl$.

Bichloride of Tin.—When protochloride of tin is heated in chlorine gas, or on distilling a mixture of 8 parts of granulated tin with 24 of bichloride of mercury, a very volatile, colourless liquid passes over, which is bichloride of tin. In an open vessel it emits dense white fumes, caused by the moisture of the air, and hence it was formerly called the *fuming liquor* of Libavius, who discovered it. At 248° it boils, and the sp. gr. of its vapour was found by Dumas to be 9·1997. With one-third of its weight of water it forms a solid hydrate, and in a larger quantity of water dissolves.

The solution of bichloride of tin, commonly called *permuriate of tin*, is much used in dyeing, and is prepared by dissolving tin in nitro-hydrochloric acid. The process requires care; for if the action be very rapid, as is sure to happen if strong acid be employed and much tin added at once, the peroxide will be spontaneously deposited as a bulky hydrate, and be subsequently redissolved with great difficulty. But the operation will rarely fail, if the acid is made with two measures of hydrochloric acid, one of nitric acid, and one of water, and if the tin is gradually dissolved, one portion disappearing before another is added. The most certain mode of preparation, however, is to prepare a solution of the protochloride, and convert it into a bichloride, either by chlorine or by gentle heat and nitric acid.

Its eq. is 128·74; symb. $Sn + 2Cl$, or $SnCl_2$.

Iodides of Tin.—The protiodide is formed by heating granulated tin with about 2½ times its weight of iodine, and is a brownish-red translucid substance, very fusible, volatile at a high temperature, and soluble in water.

Its eq. is 184·2; symb. $Sn + I$, or SnI.

The periodide is prepared by dissolving in hydriodic acid the hydrate of the peroxide precipitated by alkalies from the bichloride. It crystallizes in yellow crystals of a silky lustre, which are resolved by boiling water into hydriodic acid and peroxide of tin.

Its eq. is 310·5; symb. $Sn + 2I$, or SnI_2.

Protosulphuret of Tin.—This compound is prepared by pouring melted tin upon its own weight of sulphur, and stirring rapidly with a stick during the action; as some tin usually escapes the sulphur from the latter being rapidly expelled, the product should be pulverized, mixed with its weight of sulphur, and projected in successive portions into a hot hessian crucible, and then heated to redness. It is a brittle compound, of a bluish-grey, nearly black, colour and metallic lustre, which fuses at a red heat, and acquires a lamellated texture in cooling. It is dissolved by hydrochloric acid with evolution of hydrosulphuric acid. The same sulphuret is obtained in the moist way by adding hydrosulphuric acid to a solution of protochloride of tin.

Its eq. is 74·0; symb. $Sn + S$, or SnS.

The *Sesquisulphuret* is formed by mixing the protosulphuret in fine powder with a third of its weight of sulphur, and heating the mixture to low redness until sulphur ceases to escape. Its colour is a deep greyish yellow, it is reconverted by a strong heat into the protosulphuret, and dissolves in hydrochloric acid gas, yielding hydrosulphuric acid gas and a residue of bisulphuret of tin.

Its eq. is 164·1; symb. $2Sn + 3S$, or Sn_2S_3.

Bisulphuret of Tin, formerly called *mosaic gold*, is prepared by heating in a glass or earthen retort a mixture of 2 parts of peroxide of tin, 2 of sulphur, and 1 part of sal-ammoniac, and maintaining a low red heat until sulphurous acid ceases to be evolved. These materials are sometimes employed without sal-ammoniac, but Berzelius says that the latter is essential for obtaining the bisulphuret. The product, when successfully prepared, is in crystalline scales, and sometimes even in regular six-sided tables, of a golden yellow colour and metallic lustre. It is soluble in pure potassa and in its carbonate by boiling; but its only solvent among the acids is the nitro-hydrochloric. The bisulphuret is obtained as a bulky hydrate of a dirty yellow colour by the action of hydrosulphuric acid or hydrosulphate of ammonia on bichloride of tin in solution.

Its eq. is 90·1; symb. $Sn + 2S$, or SnS_2.

Terphosphuret of Tin.—Rose formed this compound by acting on a solution of protochloride of tin by phosphuretted hydrogen. It is readily oxidized by the action of the air.

Its eq. is 105·0; symb. $Sn + 3P$, or SnP_3.

SECTION XIV.

COBALT.—NICKEL.

COBALT.

Hist.—This metal is met with in the earth chiefly in combination with arsenic, constituting an ore from which all the cobalt of commerce is derived. It is a constant ingredient of meteoric iron, though in very small quantity. (Stromeyer.) Gregory has detected it also in many specimens of native peroxide of manganese. Its name is derived from the term *Kobold, an evil spirit*, applied to it by the German miners at a time when they were ignorant of its value, and considered it unfavourable to the presence of valuable metals.

Prep.—When native arseniuret of cobalt is broken into small pieces, and exposed in a reverberatory furnace to the united action of heat and air, its elements are oxidized, most of the arsenious acid is expelled in the form of vapour, and an impure oxide of cobalt, called *zaffre*, remains. This is dissolved in hydrochloric acid, and a current of hydrosulphuric acid gas is transmitted through the solution until the arsenious acid is completely separated in the form of orpiment. The filtered liquid is then boiled with a little nitric acid, in order to convert the protoxide into peroxide of iron, and an excess of carbonate of potassa is added. The precipitate, consisting of peroxide of iron and carbonate of protoxide of cobalt, after being well washed with water, is digested in a solution of oxalic acid, which dissolves the oxide of iron, and leaves the oxide of cobalt in the form of an insoluble oxalate. (Laugier.) Another process is, to add, by degrees, the native arseniuret, finely powdered, to 3 parts of bisulphate of potash, fused in a moderate heat, gradually increasing the fire till no more white fumes appear. The mass, when cold, is powdered and boiled in water as long as anything dissolves. The solution is free from arsenic. It is precipitated by a fixed alkaline carbonate, and the precipitate treated as above with oxalic acid. Should the oxalate contain, as it commonly does, a trace of nickel, it is to be dissolved in ammonia, and the solution exposed to the air in a deep vessel till the excess of ammonia is dissipated, when the double oxalate of ammonia and nickel is deposited in an insoluble apple-green powder, while the corresponding salt of cobalt remains in solution, giving to the liquid a deep claret-red colour. This solution, digested with potash, yields peroxide of cobalt as a brownish-black precipitate, which is quite pure. It dissolves readily in hydrochloric acid, with disengagement of chlorine, and yields a solution of protochloride, which is precipitated by carbonate of soda, and the precipitate acted on by oxalic acid. On heating the pure oxalate thus obtained in a retort from which atmospheric air is excluded, a large quantity of carbonic acid is evolved, and a black powder, metallic cobalt, is left. (Thomson in Annals of Philosophy, N. S., i.) The pure metal is easily procured also by passing a current of dry hydrogen gas over oxide of cobalt heated to redness in a tube of porcelain. In this state it is porous, and if formed at a low temperature it inflames spontaneously, as stated in the section on Iron.

Another method has lately been proposed by Wöhler for extracting pure cobalt from the arseniuret. 1 part of the ore is fused with 3 parts of pearlash and 3 parts of sulphur, by which means the arsenic is converted into a soluble arseniate, while the cobalt forms an insoluble sulphuret. After this has been well boiled in water, it is dissolved in nitric acid, and yields a solution free from arsenic, from which iron and nickel may be separated, if present, as above directed.

Prop.—A brittle metal, of a reddish-grey colour, and weak metallic lustre. Its density, according to my observation, is 7·834. It fuses at a heat rather lower than iron, and when slowly cooled it crystallizes. It has long been considered to be attracted by the magnet, but Faraday denies that it possesses this property when pure. It undergoes little change in the air, but absorbs oxygen when heated in open vessels. It is attacked with difficulty by sulphuric or hydrochloric acid, but is readily oxidized by means of nitric acid. Like iron and the other metals of this order, it decomposes water at a red heat with disengagement of hydrogen gas. (Despretz.)

According to the analyses by Rothoff of the oxides of cobalt, its equivalent is inferred to be 29·5. (An. of Phil. iii. 356.) Its symb. is Co. The composition of its compounds described in this section is as follows:—

	Colbalt.			Equiv.	Formulæ.
Protoxide .	29·5	1 eq.+Oxygen	8	1 eq.= 37·5	Co+O or CoO.
$\frac{4}{3}$ Oxide .	88·5	3 eq.+ . .	32	4 eq.=120·5	3Co+4O or Co_3O_4.
Peroxide .	59·0	2 eq.+ . .	24	3 eq.= 83·0	2Co+3O or Co_2O_4.
Chloride .	29·5	1 eq.+Chlorine	35·42	1 eq.= 64·92	Co+Cl or CoCl.
Protosulphuret	29·5	1 eq.+Sulphur	16·1	1 eq.= 45·6	Co+S or CoS.
Sesquisulphuret	59	2 eq.+ . .	48·3	3 eq.=107·3	2Co+3S or Co_2S_3.
Bisulphuret .	29·5	1 eq.+ . .	32·2	2 eq.= 61·7	Co+2S or CoS_2.
Subphosphuret	88·5	3 eq.+Phosph.	31·4	2 eq.=119·9	3Co+P or Co_3P.

Protoxide of Cobalt.—Prepared by decomposing carbonate of the protoxide by heat in a vessel from which atmospheric air is excluded. It is of an ash-grey colour, and is the basis of the salts of cobalt, most of which are of a pink hue. When heated to redness in open vessels it absorbs oxygen, and is converted into the peroxide. It is easily recognised by giving a blue tint to borax when melted with it; and is employed in the arts, in the form of smalt, for communicating a similar colour to glass, earthenware, and porcelain. It is precipitated from its salts by pure potassa as a blue hydrate, which absorbs oxygen from the air, and gradually acquires a dirty green tint. Pure ammonia likewise causes a blue precipitate, which is redissolved by the alkali if in excess. It is thrown down as a pale pink carbonate by carbonate of potassa, soda, or ammonia; but an excess of the last redissolves it with facility. Hydrosulphuric acid produces no change, unless the solution is quite neutral, or the oxide is combined with a weak acid. Alkaline hydrosulphates always precipitate it as a black protosulphuret of cobalt. Its eq. is 37·5; symb. Co + O, $\dot{Co}$, or CoO.

$\frac{4}{3}$ *Oxide of Cobalt.*—It is said that when protoxide of cobalt, or the nitrate, carbonate, or oxalate of that oxide, is gently ignited in an open fire, peroxide of cobalt results; but M. Hess has lately shewn that the oxide then obtained is analogous in composition to the red oxide of manganese. The peroxide of cobalt is converted into it, with loss of oxygen, by a full red heat, whether exposed to the air or not; so that of the oxides of cobalt it is the most stable. The same compound is obtained as a dirty green hydrate by the action of the air on the hydrated protoxide. It is probably a compound of peroxide and protoxide of cobalt, since 3Co + 4O obviously contain the elements $CoO + Co_2O_3$. This intermediate oxide is of a dark brown colour, and does not unite with acids or alkalies. (Pog. Annalen, xxvi. 542.)

Its eq. is 120·5; symb. $CoO + Co_2O_3$.

Peroxide.—Is obtained as a black hydrate containing 2 eq. of water, $Co_2O_3 + 2HO$, when chloride of cobalt in solution is decomposed by hypochlorite of lime, or chlorine is transmitted into water in which hydrated protoxide of cobalt is suspended. In this case,

3 eq. Protoxide and	1 eq. Chlorine	yield	1 eq. Peroxide and	1 eq. Chloride
$3CoO$	Cl		Co_2O_3	$CoCl$

This hydrate has a black colour and yields the black anhydrous peroxide by exposure to a heat of 600° or 700°; but it is difficult to drive off all the water, without also losing oxygen. It combines with none of the acids, and when digested with hydrochloric acid it emits chlorine gas, and chloride of cobalt is generated.

Its eq. is 83·0; symb. $2Co + 3O$, $\overset{\cdots}{\underline{Co}}$, or Co_2O_3.

When a salt of cobalt is treated with pure ammonia in close vessels, part of the cobalt is dissolved, and part subsides in form of a blue powder. On admitting atmospheric air, this substance passes to a higher state of oxidation, and is gradually dissolved. If nitrate of cobalt is used, a double salt may be obtained in crystals, which L. Gmelin, to whom we are indebted for these remarks, believes to consist of nitrate and *cobaltate* of ammonia. Of the existence of this acid, however, Winkelblech, who has examined the subject, could obtain no evidence. (Lieb. An. xiii. 253.)

Chloride of Cobalt.—It is obtained in solution on dissolving metallic cobalt, its protoxide or either of the other oxides, in hydrochloric acid, with evolution of hydrogen gas with the first and of chlorine with the latter. It yields a pink-coloured solution, and by evaporation small crystals of the same colour containing water of crystallization. When deprived of water its colour is blue, a character on which is founded its use as a sympathetic ink: when letters are written with a dilute solution of the chloride, the colour is so pale that it is invisible in the cold; but on heating gently the letters appear of a blue colour, and disappear as soon as the chloride has recovered its moisture from the atmosphere. When iron or nickel is present the dry chloride of cobalt is green instead of blue.

Its eq. is 64·92; symb. $Co. + Cl$, or $CoCl$.

Sulphurets.—Cobalt appears to unite with sulphur in three proportions; the first being a protosulphuret, the second a sesquisulphuret, and the third a bisulphuret. The protosulphuret may be formed in the dry way by throwing fragments of sulphur on red-hot cobalt, or by igniting protoxide of cobalt with sulphur; or finally, by fusing the arseniuret of cobalt with 3 parts of pearlash and 3 parts of sulphur (Wöhler); and it is thrown down as a black precipitate from the salts of cobalt by alkaline hydrosulphates, or even by hydrosulphuric acid gas if the salt is quite neutral, or the oxide united with any of the feebler acids. It has a grey colour, a metallic lustre, and a crystalline texture.

Its eq. is 45·6; symb. $Co + S$, or CoS.

Arfwedson has observed that when hydrogen gas is transmitted over sulphate of oxide of cobalt heated to redness, water and sulphurous acid are evolved, and a compound remains, called an *oxy-sulphuret*, consisting of oxide of cobalt united with sulphuret of cobalt. When this substance is exposed to hydrosulphuric acid gas at a red heat, the oxide is decomposed, and the sesquisulphuret is formed.

Its eq. is 107·3; symb. $2Co + 3S$, or Co_2S_3.

The bisulphuret is prepared, according to Setterberg, by heating 2 parts of carbonate of oxide of cobalt intimately mixed with 3 parts of sulphur. The process is conducted in a glass retort, and the heat continued as long as sulphur is expelled; but the temperature should not be suffered to reach that of redness.

Its eq. 61·7; symb. $Co + 2S$, or CoS_2.

Subphosphuret of Cobalt.—Rose obtained this phosphuret by the action of hydrogen gas on subphosphate of oxide of cobalt heated in a tube, water being also generated. In this case

$$\begin{array}{ccccc} \text{1 eq. Phosphate and} & \text{8 eq. Hydrogen} & & \text{1 eq. Phosphuret and} & \text{8 eq. Water} \\ 3(Co+O)+(P+5O) & 8H. & \text{yield} & 3Co+P & 8\,(H+O). \end{array}$$

This phosphuret is pulverulent and of a grey colour, and is also obtained by the action of phosphuretted hydrogen gas on chloride of cobalt.

Its eq. is 119·9; symb. $3CO + P$, or Co_3P.

NICKEL.

Hist. and Prep.—NICKEL is a constituent of meteoric iron, and, according to Gregory, of native peroxide of manganese; but its principal ore is the copper-coloured mineral of Westphalia, termed *küpfernickel, copper-nickel; nickel* being an epithet of detraction, applied by the old German miners, because the mineral looked like an ore of copper, and yet they could extract none from it. The preparations of nickel may either be prepared from copper-nickel, which is an arseniuret of nickel containing small quantities of sulphur, copper, cobalt, and iron, or from the artificial arseniuret called *speiss*, a metallurgic production obtained in forming smalt from the roasted ore of cobalt. Various processes have been devised for procuring a pure salt of nickel, but the following, proposed by Wöhler, is one of the best. 1 part of the ore is to be fused with 3 parts of pearlash and 3 parts of sulphur. The arsenic forms, with the sulphur and potash, a soluble compound, and the nickel forms with the sulphur an insoluble sulphuret. This is well washed with water, and dissolved in nitric acid; and the solution, after any lead, copper, or bismuth that may be present have been precipitated by a current of sulphuretted hydrogen, is precipitated by caustic or carbonated potash or soda. The washed precipitate is now acted on by an excess of oxalic acid, which forms, with the peroxide of iron that is generally present, a soluble, and with the oxide of nickel an insoluble oxalate, which of course includes any cobalt that the ore may have contained. The oxalate is now dissolved in an excess of ammonia, and the solution exposed to the air. As the ammonia escapes, the nickel is deposited as an insoluble double oxalate, while the cobalt remains dissolved as a soluble double oxalate, of the metallic oxide with ammonia. The nickel salt, being ignited, leaves oxide, which may be reduced by heating with charcoal, or dissolved in acid, and again converted into oxalate, which this time is free from cobalt, and appears as a pale apple-green powder. The oxalate of nickel, being well washed, dried, and ignited in a closed crucible, with an aperture for the escape of gas, leaves metallic nickel, which, if the heat be very intense, is fused into a button.

Wöhler gives another process, which is said to be preferable to the above. It consists in projecting the finely powdered ore along with 2 parts of nitre and 1 of carbonate of potash, by degrees, into a red-hot crucible, and finally raising the heat for a good while. The arsenic is oxidized, yielding arsenic acid, which unites with the potash, while the nickel is also oxidized, and forms oxide of nickel, which is left undissolved when the mass is lixiviated with water. This oxide is pure, except from cobalt and iron, which must be separated as above. When these metals are not present, the oxide may be at once reduced by heating with charcoal, and yields pure nickel.

Prop.—It is of a white colour, intermediate between that of tin and silver. It has a strong metallic lustre, and is both ductile and malleable. It is attracted by the magnet, and like iron may be rendered magnetic at common temperatures, but loses this power at 630°. (Faraday.) Its sp. gr. after fusion is about 8·279, and is increased to near 9·0 by hammering. Nickel is much used as an ingredient in the alloy called German or Berlin silver.

Nickel is very infusible, but less so than pure iron. It suffers no change at common temperatures by exposure to air and moisture; but it absorbs oxygen at a red heat, though not rapidly, and is partially oxidized. It decomposes water at the same temperature. Hydrochloric and sulphuric acids act upon it with difficulty; but by nitric acid it is readily oxidized, and forms a nitrate of the protoxide of nickel.

From the analyses of the oxides of nickel by Rothoff and Tupputi the eq. of nickel may be estimated at 29·5. Its symb. is Ni. The composition of its compounds described in this section is as follows:—

	Nickel.				Equiv.	Formulæ.
Protoxide .	29·5	1 eq.+Oxygen	8	1 eq.=	37·5	$Ni+O$ or NiO.
Peroxide .	59·0	2 eq.+do.	24	3 eq.=	83·0	$2Ni+3O$ or Ni_2O_3.
Chloride .	29·5	1 eq.+Chlorine	35·42	1 eq.=	64·92	$Ni+Cl$ or $NiCl$.
Disulphuret .	59	2 eq.+Sulphur	16·1	1 eq.=	75·1	$2Ni+S$ or Ni_2S.
Protosulphuret	29·5	1 eq.+do.	16·1	1 eq.=	45·6	$Ni+S$ or NiS.
Subphosphuret	88·5	3 eq.+Phosph.	31·4	1 eq.=	119·9	$3Ni+P$ or Ni_3P.

Protoxide of Nickel.—This oxide has lately been found by Genth in considerable quantity among the products of a copper smelting-furnace at Riechelsdorf. It forms minute octohedral crystals, resembling the native suboxide of copper, which are quite insoluble in acids, but dissolve readily when fused with bisulphate of potash. They were found to be chemically pure protoxide of nickel. It may be formed by heating the carbonate, oxalate, or nitrate to redness in an open vessel, and is then of an ash-grey colour; but after exposure to a white heat, its colour is a dull olive-green. It is not reducible by heat unaided by combustibles. It is not attracted by the magnet. It is a strong alkaline base, and nearly all its salts have a green tint. It is precipitated as a hydrate of a pale-green colour by the pure alkalies, but is redissolved by ammonia in excess; as a pale green carbonate by alkaline carbonates, but is dissolved by an excess of carbonate of ammonia; and as a black sulphuret by alkaline hydrosulphates. Hydrosulphuric acid occasions no precipitate, unless the solution is quite neutral, or the oxide combined with a weak acid.

Its eq. is 37·5; symb. $Ni + O$, $\dot{Ni}$, or NiO.

Peroxide.—It is formed by transmitting chlorine gas through water in which the hydrate of the protoxide is suspended. It has a black colour, does not unite with acids, is decomposed by a red heat, and with hot hydrochloric acid forms the chloride with disengagement of chlorine gas.

Its eq. is 83·0; symb. $2Ni + 3O$, $\overset{\cdots}{\underline{Ni}}$, or Ni_2O_3.

Thenard succeeded in preparing a peroxide by the action of peroxide of hydrogen on hydrated protoxide of nickel; but it is uncertain whether the composition of this peroxide is identical with that above described, or different. Two sub-oxides have likewise been enumerated, but their existence is exceedingly problematical.

Chloride of Nickel.—This compound is formed by acting with hydrochloric acid on metallic nickel, its protoxide or peroxide, hydrogen gas being evolved with the former, and chlorine with the latter. It forms an emerald-green solution, and by evaporation yields crystals of the same tint, which lose water or deliquesce according as the air is dry or moist. In its anhydrous state it is yellow; but a small admixture with cobalt causes a green tint. At a low red heat it sublimes and condenses in brilliant scales of a gold-yellow colour.

Its eq. is 64·92; symb. $Ni + Cl$, or $NiCl$.

Protosulphuret of nickel is formed by processes similar to those described for preparing protosulphuret of cobalt. The precipitated sulphuret is dark brown or nearly black, and is dissolved by hydrochloric acid with evolution of hydrosulphuric; while that procured in the dry way is of a greyish-yellow colour, and requires for solution nitric or nitro-hydrochloric acid. It occurs as a natural production in very delicate acicular crystals, the *haarkies* of the Germans.

Its eq. is 45·6; symb. $Ni + S$, or NiS.

Arfwedson obtained the disulphuret by transmitting hydrogen gas over sulphate of oxide of nickel at a red heat. It is of a lighter yellow and more fusible than the other.

Its eq. is 75·1; symb. $2Ni + S$, or Ni_2S.

Subphosphuret of Nickel.—Rose obtained it by the action of hydrogen gas on subphosphate of oxide of nickel, the same change ensuing as with cobalt; and it is generated by the action of phosphuretted hydrogen gas on chloride of nickel. It has a black colour, is insoluble in hydrochloric acid, but dissolves in nitric acid. Heated by the blowpipe, it burns with flame.

Its eq. is 119·9; symb. $3Ni + P$, or Ni_3P.

ORDER II.

METALS WHICH DO NOT DECOMPOSE WATER AT ANY TEMPERATURE, AND THE OXIDES OF WHICH ARE NOT REDUCED TO THE METALLIC STATE BY THE SOLE ACTION OF HEAT.

SECTION XV.

ARSENIC.

Hist. and Prep.—Metallic arsenic sometimes occurs native, but more frequently it is found in combination with other metals, and especially with cobalt and iron. On roasting these arsenical ores in a reverberatory furnace, the arsenic, from its volatility, is expelled, combines with oxygen as it rises, and condenses into thick cakes on the roof of the chimney. The sublimed mass, after being purified by a second sublimation, is the virulent poison known by the name of *arsenic* or *white oxide of arsenic.* From this substance the metal itself is procured by heating it with charcoal. The most convenient process is to mix the white oxide with about twice its weight of black flux, and expose the mixture to a red heat in a hessian crucible, over which is luted an empty crucible for receiving the metal. The reduction is easily affected, and metallic arsenic collects in the upper crucible, which should be kept cool for the purpose of condensing the vapour.

Prop.—An exceedingly brittle metal, of a strong metallic lustre and white colour, running into steel grey. Its structure is crystalline, and when slowly sublimed it is said to crystallize in rhombohedrons. It sp. gr. is 5·8843. When heated to 356° it sublimes without previously liquefying, for its point of fusion is far above that of its sublimation, and has not hitherto been determined. Its vapour has a strong odour of garlic; a property which affords a distinguishing character for metallic arsenic, as it is not possessed by any other metal, with the exception perhaps of zinc, which is said to emit a similar odour when thrown in powder on burning charcoal; an effect, however, most probably due to the presence of arsenic in the zinc. In close vessels it may be sublimed without change; but if atmospheric air be admitted, it is rapidly converted into the white oxide. According to Hahneman it is slowly oxidized and dissolved by being boiled in water. In general it speedily tarnishes by exposure to air and moisture, acquiring upon its surface a dark film, which is extremely superficial;

but Berzelius remarks that he has kept some specimens in open vessels for years without loss of lustre, while others are oxidized through their whole substance, and fall into powder. It has lately been suggested (Liebig's Annalen, 1840) that this effect is owing to the presence of potassium, derived from the black flux. The arsenic sublimed from the cakes which occur in commerce is permanent in the air. The product of this spontaneous oxidation, which is known abroad under the name of *fly-powder*, is supposed by Berzelius to be an oxide; but it is more generally regarded as a mixture of white oxide and metallic arsenic.

The eq. of arsenic, as inferred by Berzelius from the composition of arsenious and arsenic acids, is 37·7; but this number necessitates, in most of the compounds of arsenic, the assumption of the presence of 2 eq. of the metal. Under the head of Phosphorus, it has been shewn that there is no good reason for admitting 2 eq., instead of 1 eq., of phosphorus in its compounds; and the singular analogy existing between phosphorus and arsenic renders it necessary to apply the same rule to both. I shall therefore double the number given by Berzelius, and adopt 75·4 as the eq. of arsenic. Its symb. is As. The compounds of this metal described in this section are thus constituted:—

	Arsenic.			Equiv.	Formulæ.
Arsenious Acid	75·4	1 eq.+Oxygen	24	3 eq.= 99·4	$As+3O$ or AsO_3.
Arsenic Acid .	75·4	1 eq.+do.	40	5 eq.=115·4	$As+5O$ or AsO_5.
Bichloride .	75·4	1 eq.+Chlorine	70·84	2 eq.=146·24	$As+2Cl$ or $AsCl_2$.
Terchloride .	75·4	1 eq.+do.	106·26	3 eq.=181·66	$As+3Cl$ or $AsCl_3$.
Periodide .	75·4	1 eq.+Iodine	631·5	5 eq.=706·9	$As+5I$ or AsI_5.
Terbromide .	75·4	1 eq.+Bromine	235·2	3 eq.=313·6	$As+3Br$ or $AsBr_3$.
Bihyduret .	75·4	1 eq.+Hydrogen	2	2 eq.= 77·4	$As+2H$ or AsH_2.
Arseniur. Hydro.	75·4	1 eq.+do.	3	3 eq.= 78·4	$As+3H$ or AsH_3.
Bisulphuret .	75·4	1 eq.+Sulphur	32·2	2 eq.=107·6	$As+2S$ or AsS_2.
Tersulphuret .	75·4	1 eq.+do.	48·3	3 eq.=123·7	$As+3S$ or AsS_3.
Persulphuret .	75·4	1 eq.+do.	80·5	5 eq.=155·9	$As+5S$ or AsS_5.

Arsenious Acid.—Prep.—This compound, frequently called *white arsenic* and *white oxide of arsenic*, is always generated when arsenic is heated in open vessels, and may be prepared by digesting the metal in dilute nitric acid. The white arsenic of commerce is derived from the native arseniurets of cobalt, being sublimed during the roasting of these ores for the preparation of zaffre, and it is purified by a second sublimation in iron vessels.

Prop.—It is commonly sold in the state of a fine white powder; but when first sublimed, it is in the form of brittle masses, more or less transparent, colourless, of a vitreous lustre, and conchoidal fracture. This glass, which may also be obtained by fusion, gradually becomes opaque without undergoing any apparent change of constitution, either with respect to water or any other substance; but the change is certainly promoted by exposure to the atmosphere. Its sp. gr. is 3·7. At 380° it is volatilized, yielding vapours which do not possess the odour of garlic, and which condense unchanged on cold surfaces. Its point of fusion is rather higher than that at which it sublimes; and therefore, in order to be fused, it must either be heated under pressure, or its temperature be suddenly raised above 380°. Arsenious acid is *dimorphous*, that is, susceptible of assuming two crystalline forms belonging to different systems of crystallization. By slow sublimation in a glass tube it is always obtained in distinct octohedral crystals of adamantine lustre and perfectly transparent. Its unusual form is that of six-sided scales derived from a rhombic prism, and was first lately found by Wöhler among the products in a manufacture of smalt: the conditions for enabling it to assume this form are unknown, and by subliming the crystals, they crystallized in octohedrons. (An. de Ch. et Ph. li. 201.)

The taste of arsenious acid is stated differently by different persons. It is commonly thought to be acrid; but I am satisfied from personal observation that it may be deliberately tasted without exciting more than a very faint impression of sweetness, and perhaps of acidity. The acrid taste ascribed to it has probably been confounded with the local inflammation, by which its application, of some continuance, is followed. (Christison on Poisons.) It reddens vegetable blue colours feebly, an effect which is best shewn by placing the acid in powder on moistened litmus paper. It combines with salifiable bases, forming salts which are termed *arsenites*.

According to the experiments of Klaproth and Bucholz, 1000 parts of boiling water dissolve 77·75 of arsenious acid; and the solution, after having cooled to 60° F., contains only thirty parts. The same quantity of water at 60°, when mixed with the acid in powder, dissolves only two parts and a half. Guibourt has lately observed that the transparent and opaque varieties of arsenic differ in solubility. He found that 100 parts of temperate water dissolve, during 36 hours, 9·6 of the transparent, and 12·5 of the opaque variety; that the same quantity of boiling water dissolves 97 parts of the transparent variety, retaining 18 when cold, but takes up 115 of the opaque variety, and retains 29 on cooling. By the presence of organic substances, such as milk or tea, its solubility is materially impaired. (Christison on Poisons.)

When metallic arsenic is sharply heated with hydrate of potassa, pure hydrogen gas is evolved, and a mass is left consisting of arseniuret of potassium and arsenite of potassa; facts, which prove that a portion of arsenic is oxidized, and derives its oxygen partly from water and partly from potassa. If the heat is raised to redness, the arsenious acid is resolved into arsenic acid and metal, the former remaining as an arseniate, while the latter is expelled. Similar phenomena ensue with the hydrates of soda, baryta, and lime; except that with the two latter no arsenic acid is produced. (Soubeiran in An. de Ch. et Ph. xliii. 410.)

Its eq. is 99·4; symb. $As + 3O$, $\dddot{As}$, or AsO_3.

The frequent exhibition of arsenious acid as a poison renders the detection of this compound an object of great importance to Medical Practitioners as well as to the Chemist. In this as in all similar inquiries, the object to be held in view is the discovery of a few decisive characters, by means of which the poison may be distinguished from all other bodies, and, when present but in small quantities, either in pure water or in any fluids likely to be met with in the stomach, may with certainty be detected. The attention should be fixed on one or two tests of admitted value, and all others be set aside. With this feeling I shall indicate the mode of applying the four principal tests, namely, the ammoniaco-nitrate of silver, ammoniaco-sulphate of copper, hydrosulphuric acid, and hydrogen gas.

1. Arsenious acid is not precipitated by nitrate of oxide of silver unless an alkali is present to neutralize the nitric acid. Ammonia is commonly employed for the purpose; but as arsenite of oxide of silver is very soluble in ammonia, an excess of the alkali would retain the arsenite in solution. To remedy this inconvenience, Hume, of Long Acre, proposed to employ the ammoniacal nitrate of silver, which is made by dropping ammonia into a rather strong solution of lunar caustic, till the oxide of silver at first thrown down is *nearly* all dissolved. The liquid thus prepared contains the precise quantity of ammonia which is required; and when mixed with arsenious acid, two neutral salts result, the soluble nitrate of ammonia, and the insoluble yellow arsenite of oxide of silver. Ammoniacal nitrate of silver likewise diminishes the risk of fallacy that might arise from the presence of phosphoric acid. Phosphate of oxide of silver is so very soluble in ammonia, that when a neutral phosphate is mixed with the ammoniacal nitrate of silver, the resulting phosphate is held almost entirely in solution by the free ammonia.

This test, however, even in its improved state, is still liable to objection. For when arsenious acid in small proportion is mixed with sea salt, or animal and vegetable infusions, the arsenite of oxide of silver either does not subside at all, or is precipitated in so impure a state that its characteristic colour cannot be distinguished. Several methods have been proposed for obviating this source of fallacy; but

Christison has shewn that this test, taken singly, cannot be relied on in practice.

2. Ammoniacal sulphate of copper, which is made by adding ammonia to a solution of sulphate of oxide of copper until the precipitate at first thrown down is nearly all redissolved, occasions with arsenious acid a green precipitate, which has been long used as a pigment under the name of *Scheele's green.* This test, though well adapted for detecting arsenious acid dissolved in pure water, is very fallacious when applied to mixed fluids. Christison has proved that ammoniacal sulphate of copper produces in some animal and vegetable infusions, containing no arsenic, a greenish precipitate, which may be mistaken for Scheele's green; whereas in other mixed fluids, such as tea and porter, to which arsenic has been previously added, it occasions none at all, if the arsenious acid is in small quantity. In some of these liquids, a free vegetable acid is doubtless the solvent; for arsenite of oxide of copper is also dissolved by tannic acid, and perhaps by other vegetable as well as some animal principles. This and the preceding test are only valuable when applied to a pure solution of arsenious acid in water; but in this way, as we shall see, they may be very usefully employed.

3. When a current of hydrosulphuric acid gas is conducted through a solution of arsenious acid, the fluid immediately acquires a yellow colour, and in a short time becomes turbid, owing to the formation of orpiment, the tersulphuret of arsenic. The precipitate is at first partially suspended in the liquid; but as soon as free hydrosulphuric acid is expelled by heating the solution, it subsides perfectly, and may easily be collected on a filter. One condition, however, must be observed in order to ensure success, namely, that the liquid does not contain a free alkali; for sulphuret of arsenic is dissolved with remarkable facility by pure potassa or ammonia. To avoid this fallacy, it is necessary to acidulate the solution with a little acetic or hydrochloric acid. Hydrosulphuric acid likewise acts on arsenic in all vegetable and animal fluids if previously boiled, filtered, and acidulated.

But it does not necessarily follow, because hydrosulphuric acid causes a yellow precipitate, that arsenic is present; since there are not less than four other substances, namely, selenium, cadmium, tin, and antimony, the sulphurets of which, judging from their colour alone, might possibly be mistaken for orpiment. From these, and all other substances whatever, the sulphuret of arsenic may be thus distinguished:—On drying the sulphuret, mixing it with black flux, and heating the mixture contained in a glass tube to redness by means of a spirit-lamp, decomposition ensues, and a metallic crust of an iron-grey colour externally, and crystalline on its inner surface, is deposited on the cool part of the tube. This character alone is quite satisfactory; but it is easy to procure additional evidence, by reconverting the metal into arsenious acid, so as to obtain it in the form of resplendent octohedral crystals. This is done by holding that part of the tube to which the arsenic adheres about three-fourths of an inch above a very small spirit-lamp flame, so that the metal may be slowly sublimed. As it rises in vapour, it combines with oxygen, and is deposited in crystals within the tube. The character of these crystals with respect to volatility, lustre, transparency, and form, is so exceedingly well marked, that a practised eye may safely identify them, though their weight should not exceed the 100th part of a grain. This experiment does not succeed unless the tube be quite clean and dry.

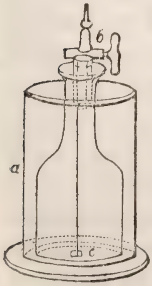
The only circumstance which occasions a difficulty in the preceding process is the presence of organic substances, which cause the precipitate to subside imperfectly, render filtration tedious, and froth up inconveniently during the reduction. Hence, if so abundant as materially to impede filtration and prevent the liquid from becoming clear, they should be removed before hydrosulphuric acid is employed. This is often sufficiently effected by acidulating with acetic acid, by which caseous and albuminous substances are coagulated; but a more complete separation is accomplished by evaporating the solution at a moderate heat to dryness, redissolving anew by boiling successive portions of distilled water on the residue, and then filtering the solution after it has cooled. Most of the organic matters are thus rendered insoluble. It is of course necessary towards the close of the desiccation to guard against too high a temperature, since otherwise the arsenic itself might be expelled. (Christison on Poisons, 2nd edition, 252.)

The black flux employed in the processes for reducing arsenic, is prepared by deflagrating a mixture of bitartrate of potassa with rather less than half its weight of nitre. The nitric and tartaric acids undergo decomposition, and the solid product is charcoal derived from tartaric acid, and pure carbonate of potassa. As it contains a deliquescent salt, it should be kept in well-stopped bottles. When this substance is employed in the reduction of arsenious acid or its salts, the charcoal is of course the decomposing agent; but the alkali is of use in retaining the arsenious acid until the temperature is sufficiently high for its decomposition. With sulphuret of arsenic, on the contrary, the alkali is the active principle, the potassium of which unites with sulphur and liberates the arsenic; but the charcoal operates usefully by facilitating the decomposition of the alkaline carbonate. The whole of the arsenic, however, is not sublimed; but part of it enters into union with potassium, and remains with the flux.

Perhaps a better flux for reducing the sulphuret of arsenic is the mixture, recommended by Fresenius and Von Babo, of 3 parts of dried carbonate of soda, and 1 part of cyanide of potassium, prepared by Liebig's process. 12 parts of this flux are mixed with one of the dried sulphuret, and the mixture placed in a tube, through which is passed a current of carbonic acid gas. The mixture is heated to redness by a spirit-lamp, and the reduced arsenic is carried by the current of gas to a point somewhat beyond the flame, where it forms a ring, the brilliancy of which, owing to the absence of oxygen in the tube, remains unimpaired.

4. For the application of hydrogen in testing for arsenic we are indebted to the ingenuity of Marsh (Edinburgh New Phil. Journ., October, 1836). Its employment is dependent on the fact, that whenever hydrogen in the nascent state is brought into contact with any compound of oxygen and arsenic, the latter is instantly decomposed, and water and a gaseous compound of arsenic and hydrogen, the arseniuretted hydrogen, are generated. If the gas be inflamed as it escapes into the air through a fine tube, it burns with the production of the vapour of water, while metallic arsenic or arsenious acid is deposited, according as the supply of oxygen be more or less abundant. Hence, if a piece of cold window-glass be held in the flame, its surface is instantly covered with a thin coating of metallic arsenic; but if the flame be made to burn in the centre of a glass tube open at both extremities, the inner surface of the latter is covered in the course of half a minute with arsenious acid. If the tube be held obliquely against it, both depositions take place, and on bringing the tube, while still warm, to the nose, a peculiar odour of arsenic is readily perceived.

The experiment is made in the following manner:—The suspected substances, if in the solid form, such as bread, must first be boiled with a few ounces of distilled water, and the clear solution while still hot is to be separated from the solid parts by filtration. The same process must be adopted with very thick soups, or the contents of the stomach; while thin soups, wine, beer, coffee, tea, and similar fluids require no previous preparation. The liquid is then mixed with a few ounces of dilute sulphuric acid, and introduced into the apparatus represented by the accompanying woodcut. This consists of two parts, a cylindrical glass vessel *a*, and a capped bell jar furnished with a stop-cock and small gas-

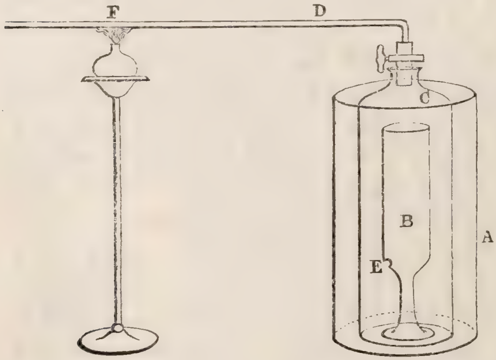


burner; to the stop-cock is suspended a string, to which a fragment of zinc *c*, reaching nearly to the bottom of the bell jar, is attached. The stop-cock *b* being open, when the liquid to be examined is poured into *a*, it rises in the bell-jar, and so much must be used that the latter is almost full. By the action of the dilute acid on the zinc hydrogen is rapidly evolved, and after permitting a small quantity to escape in order to ensure the removal of atmospheric air from the vessel, the stop-cock is turned, and the gas allowed to accumulate in the bell jar. On burning it the presence of arsenic is readily recognized by the characters above stated, and by the light blue tint it communicates to the flame. The extreme delicacy of this method has been recently amply attested by Liebig and Mohr in their valuable journal (Lieb. Annal. xxiii. 217). To avoid every source of fallacy, however, several precautions are necessary: the most important are—to ensure the perfect purity of the reagents used, as arsenic is commonly contained both in the zinc and sulphuric acid of commerce; to employ a fresh piece of zinc with each experiment, as a portion of the arsenic in the solution is deposited as a metallic crust on the zinc, which is thus rendered impure; and to prove experimentally the purity of the apparatus before each experiment. Liebig recommends that a fragment of porcelain be held in the flame instead of the window-glass, as a very thin film of metallic arsenic is better seen on the white opaque ground than on the transparent glass. He observes, too, that owing to the rapid evolution of the gas, other metals, as for example, iron, which may be contained in the solution, being carried up by the hydrogen and deposited on the porcelain, may prove a source of error to the inexperienced. For this reason he recommends that the gas, instead of being burnt by the jet, be transmitted through a fine tube of difficultly fusible glass; on bringing a part of the glass to a red heat by a spirit-lamp flame, the arsenuiretted hydrogen is decomposed as it passes, and the metallic arsenic is deposited just beyond the heated part of the glass, while other metals are deposited in the hot parts themselves.

The following is the method now pursued by Gregory, and which is a modification of that of Liebig:—The suspected matters, all solid parts being cut small, are first of all deprived of organic substances. This is accomplished by heating them with diluted hydrochloric acid, and gradually adding chlorate of potash, as recommended by Fresenius and Von Babo, until the whole becomes of a clear yellow colour, perfectly homogeneous and fluid. The liquid when cold is filtered, and the filtration takes place easily if the organic matter has been entirely decomposed. The filtered liquid is now evaporated in the water bath to a small bulk. It contains the arsenic in the form of arsenic acid, which is reduced to arsenious acid by adding sulphurous acid till the liquid smells permanently of that gas.

Fresenius and Von Babo recommend us now to precipitate the arsenic by hydrosulphuric acid, as tersulphuret of arsenic; to collect the precipitate, and to destroy any remains of organic matter adhering to it by heating it with nitric acid and subsequently with oil of vitriol, which chars the organic matter. The charred mass is then boiled with water, and there is thus obtained a solution of arsenious acid, entirely free from organic matter. According to these chemists, this solution is to be again precipitated by hydrosulphuric acid, and the precipitate is to be reduced by heating it in a current of carbonic acid gas, along with the flux above described. This method succeeds well in experienced hands, but it is very tedious, and Gregory therefore prefers the following adaptation of the process of Marsh and Liebig.

The solution, after being treated, if necessary, with chlorate of potash and hydrochloric acid, and in which the arsenic acid (see above) has been reduced to arsenious acid by sulphurous acid, is acidulated, after evaporation in the water bath, with so much dilute sulphuric acid that it acts moderately on zinc. It is then introduced into an apparatus of the annexed construction. It consists of a cylinder A, in which is placed a tall foot-glass B, perforated near the bottom at E, and an inverted bell jar C, provided with a stop-cock and a tube D. Some long slips of zinc being placed in the glass B, which is set in the large cylinder, the bell jar C is inverted over the glass, and the stop-cock shut. The bell jar is retained in its place by perforated weight, resting on the edges of the cylinder. The acid liquid is then poured into the cylinder and the stop-cock opened, when the liquid rises in the bell jar and covers the zinc, on which it acts, disengaging hydrogen. After the air of the apparatus has been expelled, the stop-cock is shut, when the gas, accumulating in the upper part of C, forces the liquor through the aperture at E and out of the glass and bell jar into the cylinder, leaving the zinc uncovered, when, of course, the disengagement of the gas ceases. The stop-cock being now partly opened, the



pressure of the liquid in the cylinder forces the gas through the tube, which is to be heated red-hot by a spirit-lamp at F, as soon as it is filled with pure hydrogen. By regulating the escape of gas it may be easily so managed that the liquid covers the zinc, and keeps up a slow, steady, and continuous current of gas; and if the quantity of arsenic be small, it is advisable to continue the experiment for some hours, or at least till the zinc is entirely dissolved. The arsenic is all collected at a point of the tube just beyond the flame. In this as in all similar operations, it is indispensable to try the experiment first for a quarter of an hour or half an hour with a portion of the same zinc and acid as are to be used, in order to be satisfied that these reagents as well as the apparatus are quite free from arsenic. If no trace of arsenic appear in the tube during this preliminary trial, the suspected liquid is to be introduced; and if arsenic then appear, we may be assured of its presence in the suspected matter.

The apparatus just described appears to me to be the best adapted of any for Marsh's process, and it may be employed in all cases where a continuous current of hydrogen, sulphuretted hydrogen, or carbonic acid gas is to be passed through a tube for some time. In testing for arsenic, the further end of the tube should be drawn out to a small aperture, and the gas as it escapes may be set fire to at the point of the tube, and a piece of porcelain held in the flame. It will be found that if the tube, which should be small and of hard infusible glass, has been properly heated at F, no arsenic whatever can be detected at the end of the tube, the whole being deposited just beyond the flame. Where the quantity of arsenic admits of it, several tubes may be attached in succession to the stop-cock, and a ring of arsenic obtained in each. This form of apparatus is admirably adapted for the lecture table.

It was hoped that this test might prove infallible even in the hands of inexperienced chemists; but according to a recent discovery of Mr. L. Thompson, antimony combines with hydrogen, forming with it a gaseous compound which is similar to arseniuretted hydrogen in the mode of its production, in the colour of its flame when burnt, and in the deposition of a metallic crust on a cold surface. The two gases may nevertheless be readily distinguished by decomposing them by means of heat while passing through a fine tube, as was proposed by Liebig for arseniuretted hydrogen; for although the metallic crusts are very similar, yet by attention to the directions of page 451, the crust of arsenic cannot be mistaken for that of antimony. For by bringing the spirit-lamp flame under the crust when the stream of hydrogen has ceased to pass along the tube, if it be arsenic it rapidly volatilizes and condenses again on the neighbouring cool parts of the tube; the antimonial crust, on the contrary, when thus heated, fuses, runs into small globules, and assumes the appearance of mercury. If the tube be now detached from the vessel in which the hydrogen is generated, and the flame of the spirit-lamp cautiously applied to the metal, the arsenic volatilizes without fumes, and distinct octohedral crystals of arsenious acid are formed on the upper parts of the tube; with antimony, on the contrary, dense white fumes are produced, and an amorphous white powder is deposited. The different characters of the two substances may be carried still further: if the tube be boiled in a small quantity of pure water, the arsenious acid is dissolved, and the first two tests may be successfully employed; the antimony, on the contrary, is insoluble.

Arsenic Acid.—This compound is made by dissolving arsenious acid in concentrated nitric, mixed with a little hydrochloric acid, distilling in glass till it acquires the consistence of syrup, and then exposing it in a platinum crucible for some time to a heat somewhat short of low redness, to expel the nitric acid. The acid thus prepared has a sour metallic taste, reddens vegetable blue colours, and with alkalies forms neutral salts, which are termed *arseniates.* It is much more soluble in water than arsenious acid, dissolving in five or six times its weight of cold, and in a still smaller quantity of hot water. It forms irregular grains when its solution is evaporated, but does not crystallize. If strongly heated, it fuses into a glass which is deliquescent. When urged by a very strong red heat, it is resolved into oxygen and arsenious acid. It is an active poison.

Arsenic acid is decomposed by hydrosulphuric acid gas, and yields a sulphuret of arsenic very like orpiment in colour, but containing a greater proportional quantity of sulphur. The soluble arseniates, when mixed with the nitrates of lead and silver, form insoluble arseniates, the former of which has a white, and the latter a brick-red colour. They dissolve readily in dilute nitric acid, and when heated with charcoal yield metallic arsenic.

Its eq. is 115·4; symb. $As + 5O$, $\overset{\cdot\cdot\cdot\cdot\cdot}{As}$, or AsO_5.

Bichloride of Arsenic.—It is prepared, according to Dumas, by introducing into a tubulated retort a mixture of arsenious acid with ten times its weight of concentrated sulphuric acid; and after raising its temperature to near 212°, fragments of sea-salt are thrown in by the tubular. If the salt is added in successive small portions, scarcely any hydrochloric acid gas is evolved, and the pure chloride may be collected in cooled vessels. Towards the end of the process a little water frequently passes over with the chloride; but this hydrated portion does not mix with the anhydrous chloride, but swims on its surface. The hydrate may be decomposed, and a pure chloride obtained, by distilling the mixture from a sufficient quantity of concentrated sulphuric acid. Dumas considers this compound a protochloride of arsenic, so that it is probably different from that obtained by means of corrosive sublimate. (Quarterly Journal of Science, N. S., i. 235.)

Its eq. is 146·24; symb. $As + 2Cl$, or $AsCl_2$.

Terchloride of Arsenic.—When arsenic in powder is thrown into a jar full of dry chlorine gas, it takes fire, and terchloride of arsenic is generated: and the same compound may be formed by distilling a mixture of six parts of corrosive sublimate with one of arsenic. It is a colourless volatile liquid, which fumes strongly on exposure to the air, hence called *fuming liquor of arsenic*, and is resolved by water into hydrochloric and arsenious acids. (Davy.)

Its eq. is 181·66; symb. $As + 3Cl$, or $AsCl_3$.

Periodide of Arsenic is formed by bringing its elements into contact, and promoting union by gentle heat. They form a deep red compound, which is resolved into arsenic and hydriodic acids by the action of water. (Plisson, in An. de Ch. et Ph. xxxix. 266.)

Its eq. is 706·9; symb. $As + 5I$, or AsI_5.

Terbromide of Arsenic.—The elements of this compound unite at the moment of contact, with vivid evolution of heat and light. Serullas prepared it by adding dry arsenic to bromine as long as light was emitted, the former being added in successive small quantities, to prevent the temperature from rising too high. The bromide is then distilled, and collected in a cool receiver. (An. de Ch. et Ph. xxxviii. 318.)

This compound is solid at or below 68°, liquefies between 68° and 77°, and boils at 428°. As a liquid it is transparent and slightly yellow, and yields long prisms by evaporation. By water it is resolved into arsenious and hydrobromic acids.

Its eq. is 313·6; symb. $As + 3Br$, or $AsBr_3$.

Bihyduret of Arsenic.—This compound, which is solid and of a brown colour, was discovered by Davy as well as Gay-Lussac and Thenard. The former prepared it by attaching a piece of arsenic to the negative wire during the decomposition of water by galvanism; and the French chemists, by the action of water on an alloy of potassium and arsenic.

Its eq. is 77·4; symb. $As + 2H$, or AsH_2.

Arseniuretted Hydrogen.—This gas, which was discovered by Scheele, has been studied by Proust, Trommsdorf, and others, but especially by Stromeyer. It is generally made by digesting an alloy of tin and arsenic in hydrochloric acid; but as thus prepared it is always mixed with free hydrogen. Soubeiran generated it by fusing arsenic with its own weight of granulated zinc, and decomposing the alloy with strong hydrochloric acid. The gas thus developed is quite free from hydrogen, being absorbed without residue by a saturated solution of sulphate of oxide of copper. Its sp. gravity, according to Dumas, is 2·695. It is colourless, and has a fetid odour like that of garlic. It extinguishes bodies in combustion, but is itself kindled by them, and burns with a blue flame. It instantly destroys small animals that are immersed in it, and is poisonous to man in a high degree, having proved fatal to a German philosopher, the late M. Gehlen, and others. Water absorbs one-fifth of its volume, and acquires the odour of the gas. It is altogether destitute of the properties of an acid.

Arseniuretted hydrogen is decomposed by various agents. It suffers gradual decomposition when mixed with atmospheric air, water being formed, and metallic arsenic, together with a little oxide, deposited. With nitric acid, water is generated, and a deposit of metal takes place, which is subsequently oxidized. Chlorine decomposes it instantly with disengagement of heat and light, hydrochloric acid being generated, and the metal set free. With iodine it yields hydriodic acid gas and iodide of arsenic, and sulphur and phosphorus produce analogous changes. By its action on salts of the easily reducible metals, such as silver and gold, the metal is revived, and its oxygen uniting with the elements of the gas, constitutes arsenious acid and water. With salts of copper the products are water and arseniuret of copper; and with several other metallic salts its action is similar.

Soubeiran observed that arseniuretted hydrogen in a glass tube is completely decomposed by the heat of a spirit-lamp, and that its hydrogen occupies one and a half as much space as when in combination. He has also confirmed the observation of Dumas, that when mixed with oxygen, and detonated by the electric spark, each volume of the gas, in forming water and arsenious acid, requires one and a half its volume of oxygen gas. The oxygen, therefore, is equally divided between the arsenic and hydrogen; and arseniuretted hydrogen consists of 1 eq. of arsenic and one and a half of hydrogen. By volume, it is composed of half a volume of the vapour of arsenic, and one and a half of hydrogen, condensed into one measure. (An. de Ch. et Ph. xliii. 407.)

Its eq. is 78·4; symb. $As + 3H$, or AsH_3.

Sulphurets of Arsenic.—Sulphur unites with arsenic in at least three proportions, forming compounds, two of which occur in the mineral kingdom, and are well known by the names of *realgar* and *orpiment.* Realgar or the bisulphuret may be formed artificially by heating arsenious acid with about half its weight of sulphur, until the mixture is brought into a state of perfect fusion. The cooled mass is crystalline, transparent, and of a ruby-red colour, and may be sublimed in close vessels without change.

Its eq. is 107·8; symb. $As + 2S$, or AsS_2.

Orpiment, or *sesquisulphuret* of arsenic, properly tersulphuret, may be prepared by fusing together equal parts of arsenious acid and sulphur; but the best mode of obtaining it quite pure is by transmitting a current of hydrosulphuric acid gas through a solution of arsenious acid. Orpiment has a rich yellow colour, fuses readily when heated, and becomes crystalline on cooling, and in close vessels may be sublimed without change. It is dissolved with great facility by the pure alkalies, and yields colourless solutions.

Orpiment is employed as a pigment, and is the colouring principle of the paint called *King's yellow*. Braconnot has proposed it likewise for dyeing silk, woollen, or cotton stuffs of a yellow colour; the cloth being soaked in a solution of orpiment in ammonia, and then suspended in a warm apartment. The alkali evaporates, and leaves the orpiment permanently attached to the cloth. (An. de Ch. et Ph. xii.)

Its eq. is 123·7; symb. $As + 3S$, or AsS_3.

Persulphuret of arsenic is prepared by transmitting hydrosulphuric acid gas through a moderately strong solution of arsenic acid; or by saturating a solution of arseniate of potassa or soda with the same gas, and acidulating with hydrochloric or acetic acid. The oxygen of the acid unites with the hydrogen of the gas, and persulphuret of arsenic subsides. In colour it is very similar to orpiment, is dissolved by pure alkalies, fuses by heat, and may be sublimed in close vessels without decomposition.

Its eq. is 155·9; symb. $As + 5S$, or AsS_5.

The experiments of Orfila have proved that the sulphurets of arsenic are poisonous, though in a much less degree than arsenious acid. The precipitated sulphuret is more injurious than native orpiment. The only antidote of arsenious acid is hydrated peroxide of iron (Bunsen), the effects of which have been amply tested in Germany, and lately elucidated by Dr. D. Maclagan. (Edin. Med. and Surg. Journal, 1840.) It acts by forming an insoluble arsenite or arseniate; and must be used in the moist state, without having been dried, and also in large quantity. The late edition (1840) of the Edinburgh Pharmacopœia gives a process for preparing it for this object.

SECTION XVI.

CHROMIUM.—VANADIUM.

CHROMIUM.

Hist.—Discovered in the year 1797 by Vauquelin in a beautiful red mineral, the native dichromate of oxide of lead. (An. de Ch. xxv. and lxx.) It has since been detected in the mineral called *chromate of iron*, a compound of the oxides of chromium and iron, which occurs abundantly in several parts of the Continent, in America, and at Unst in Shetland. (Hibbert.) It derived its name from χρωμα, *colour*, owing to its remarkable tendency to form coloured compounds.

Prep.—By exposing the oxide of chromium mixed with charcoal to the most intense heat of a smith's forge; but owing to its strong affinity for oxygen, the reduction is extremely difficult. A better process, that of Vauquelin, is to mix the dry oxide into a paste with oil, place the mass in a crucible lined with charcoal, lute on a cover, and to expose it for an hour to a very strong heat.

Prop.—As obtained by Vauquelin's process it has a white colour with a shade of yellow, and a distinct metallic lustre. It is brittle, very infusible, and with difficulty attacked by acids, even by the nitro-hydrochloric. Its sp. gr. has been stated at 5·9; but Thomson found it a little above 5. When fused with nitre it is oxidized and converted into chromic acid. With a smaller quantity of oxygen it forms the green oxide.

From the experiments of Berzelius and Thomson the eq. of chromic acid may be estimated at 52; and as the salts of this acid are isomorphous with the sulphates and seleniates, it is inferred that chromic acid has the same atomic constitution as sulphuric and selenic acids, or consists of 1 eq. of chromium and 3 eq. of oxygen. Berzelius has moreover remarked that when the acid is converted into the green oxide of chromium, it parts with exactly half of its oxygen. Hence, 24 deducted from 52 leaves 28 as the eq. of chromium. Its symb. is Cr. The composition of its compounds described in this section is as follows:—

	Chromium.			Equiv.	Formulæ.
Protoxide	28	1 eq.+Oxygen	8	1 eq.= 36	$Cr+O$ or CrO.
Sesquioxide	56	2 eq.+ . .	24	3 eq.= 80	$2Cr+3O$ or Cr_2O_3.
Binoxide	28	1 eq.+ . .	16	2 eq.= 44	CrO_2 or $Cr_2O_3+CrO_3$.
$\frac{3}{4}$ Oxide	84	3 eq.+ . .	32	4 eq.=116	$3Cr+4O$ or Cr_3O_4.
Chromic Acid	28	1 eq.+ . .	24	3 eq.= 52	$Cr+3O$ or CrO_3.
Nituret	84	3 eq.+Nitrogen	28	2 eq.=112	$3Cr+2N$ or Cr_3N_2.

	Chromium.			Equiv.	Formulæ.
Protochloride .	28	1 eq.+Chlorine	35·42	1 eq.= 63·42	$Cr+Cl$ or $CrCl$.
Sesquichloride .	56	2 eq.+ . .	106·26	3 eq.=162·26	$2Cr+3Cl$ or Cr_2Cl_3.
Sesquifluoride .	56	2 eq.+Fluorine	56·04	3 eq.=112·04	$2Cr+3F$ or Cr_2F_3.
Perfluoride .	Composition unknown.				
Sesquisulphuret .	56	2 eq.+Sulphur	48·3	3 eq.=104·3	$2Cr+3S$ or Cr_2S_3.
Protophosphuret .	28	1 eq.+Phosph.	15·7	1 eq.= 43·7	$Cr+P$ or CrP.
Oxy-chloride CrO_3	104	2 eq.+$CrCl_3$	106·26	1 eq.=210·26	$CrCl_3+2CrO_3$.

Protoxide of Chromium.—This oxide, lately discovered by Peligot, is as yet little known. When protochloride of chromium is acted on by potassa, there is formed a brown hydrate of the protoxide, which soon acquires a reddish colour. It is not permanent, but attracts oxygen with avidity, passing into the $\frac{3}{4}$ oxide, the hydrate of which when dried has the colour of Spanish snuff. Protoxide of chromium forms salts with acids. Peligot has described an acetate in red crystals, and a double sulphate with potash, analogous to the class of double sulphates of which the sulphate of potassa and magnesia is the type.

Its eq. is 36; symb. $Cr + O$ or CrO. The $\frac{3}{4}$ oxide above mentioned is evidently a compound of 1 eq. protoxide and 1 eq. sesquioxide, $CrO + Cr_2O_3 = Cr_3O_4$. It is analogous to the magnetic oxide of iron.

Sesquioxide of Chromium.—*Prep.*—This, the well-known green oxide of chromium, is prepared by dissolving chromate of potassa in water, and mixing it with a solution of nitrate of protoxide of mercury, when an orange-coloured precipitate, chromate of that oxide, subsides. On heating this salt to redness in an earthen crucible, the mercury is dissipated in vapour, and the chromic acid is resolved into oxygen and oxide of chromium. It may also be obtained by exposing the bichromate of potassa to a strong red heat, either alone, or, what is preferable, mixed with carbonate of potash or of soda and sal-ammoniac. In the former case half the chromic acid is reduced to green oxide, and the oxide appears in the form of small tabular crystals. In the latter, the whole of the acid is reduced, and the oxide appears as a heavy green powder. The latter is readily removed from the insoluble oxide by boiling water. Wöhler has succeeded in obtaining this oxide in fine crystals by conducting the vapour of the oxychloride of chromium (formerly terchloride of chromium) through a red-hot glass tube; when it is decomposed, oxide of chromium is deposited in fine crystals, and a mixture of oxygen and chlorine gases is evolved.

Prop.—As obtained by either of the first processes, it is a green powder; but the crystals of Wöhler are black and possess a strong metallic lustre, and are identical in form and very similar in appearance to specular iron ore: it is as hard as corundum, and has a sp. gr. of 5·21; its powder has the common green colour of oxide of chromium. (Pog. Ann. xxxiii. 341.)

It is insoluble in water, and after being strongly heated, resists the action of the most powerful acids. Deflagrated with nitre, or fused with chlorate of potassa, it is oxidized to its maximum, and is thus reconverted into chromic acid. Fused with borax or vitreous substances, it communicates to them a beautiful green colour, a property which affords an excellent test of its presence, and renders it exceedingly useful in the arts. The emerald owes its colour to the presence of this oxide.

Oxide of chromium is a salifiable base, and its salts, which have a green colour, may be easily prepared in the following manner. To a boiling solution of chromate of potassa in water, equal measures of strong hydrochloric acid and alcohol are added in successive small portions, until the red tint of the chromic acid disappears entirely, and the liquid acquires a pure green colour. On pouring an excess of pure ammonia into this solution, a pale green bulky hydrate subsides, which consists of 1 eq. of the oxide and 26 eq. of water. (Thomson.) The oxide, in this state, is readily dissolved by acids. On expelling the water by heat, the sudden approximation of the particles, which abruptly occurs at a certain temperature, causes such intense evolution of heat that the whole mass becomes vividly incandescent.

The anhydrous oxide is formed when bichromate of potassa is briskly boiled with sugar and a little hydrochloric acid. At first a brown matter falls, consisting of the acid and oxide of chromium; but subsequently the green oxide appears in the form of a finely divided powder. If the bichromate and sugar are employed without hydrochloric acid, the brown matter is the only solid product; and on boiling this compound with a little carbonate of potassa, a greenish blue carbonate of chromium, of a very fine colour, is obtained. For this mode of preparation I am indebted to my late pupil, Mr. Thomas Thomson, of Clitheroe, near Manchester.

Its eq. is 80; symb. $2Cr + 3O$, $\underline{\dddot{Cr}}$, or Cr_2O_3.

Chromic Acid.—Prep.—This acid is best prepared by adding 2 vol. of a cold saturated solution of bichromate of potash to 3 vol. of pure oil of vitriol, and allowing the mixture to cool in a closed flask, when it deposits beautiful deep red acicular crystals of chromic acid. (Warington.) These are dried by draining off the supernatant liquid, and placing the moist crystals on a porous tile, at the same time covering them with a bell jar to exclude the moisture of the air. Some fragments of quicklime may be advantageously placed in a capsule beside the crystals, to attract any moisture that may penetrate into the jar, and after 24 hours the crystals will be found sufficiently dry to be preserved, and to exhibit the remarkable properties of the acid.

But they cannot be obtained perfectly pure by one operation, some of the acid mother liquor adhering to them. They may be purified by redissolving them in the smallest possible quantity of hot water, and drying them as before; but for ordinary purposes this is not necessary, and the crystals deposited from water in the second operation are seldom so fine as those formed in the first, which are often obtained from one to two inches in length, although very slender.

When a hot saturated solution of bichromate of potash is decomposed by sulphuric acid, the chromic acid is deposited in very small acicular crystals, which may be dried on a tile as above, and when dry form a woolly mass of a bright vermillion colour. (Fritzsche.) In this form the acid is contaminated with more or less bisulphate of potash, but it is still sufficiently pure for many experiments. It may be purified, as above, by recrystallization.

Prop.—The crystals of pure chromic acid vary in colour according to their size, being dark red when large, and bright cinnibar red when small. When hot they are nearly black, but on cooling recover their red colour. They are highly deliquescent, and should be kept in sealed glass tubes. The solution of chromic acid is deep orange-red when concentrated, orange yellow when diluted. Chromic acid readily yields oxygen to oxidizable bodies, and is reduced to the green oxide. The crystals, when thrown into alcohol or ether, set those liquids on fire by the heat developed in the action; and when the combustion is over, nothing is left but green oxide of chromium. 2 eq. of the acid yield 1 eq. of green oxide and 3 eq. of oxygen. $2CrO_3 = Cr_2O_3 + O_3$. As an oxidizing agent, especially in organic chemistry, chromic acid is much employed, but it is generally used in the form of a mixture of sulphuric acid and bichromate of potash. Salicine, for example, distilled with such a mixture, is oxidized, and yields, among other products, the oil of spiræa, or hyduret of salicyle.

By the action of heat, chromic acid is resolved into oxygen and green oxide. When boiled with hydrochloric acid and alcohol it yields a chloride, and the direct solar rays have a similar effect when hydrochloric acid is present: the mutual action sets chlorine free, and hence the solution acquires the property of dissolving gold. With sulphurous acid it forms a sulphate of the oxide; and it is more or less completely converted into the oxide by being boiled with sugar, starch, or various other organic principles. It destroys the colour of indigo, and of most vegetable and animal colouring matters; a property advantageously employed in calico-printing, and which manifestly depends on the facility with which it is deprived of oxygen.

Chromic acid is characterized by its colour, and by forming coloured salts with alkaline bases. The most important of these salts are the bichromate of potassa, and the chromate of oxide of lead, the latter of which is found native in small quantity, and is easily prepared by mixing chromate of potassa with a soluble salt of lead. It is of a rich yellow colour, and is employed in the arts of painting and dyeing to a great extent. When heated to redness, it is also much used as the oxidizing agent in the ultimate analysis of organic substances. (Liebig.)

When sulphurous acid gas is transmitted into a solution of chromate or bichromate of potassa, a brown precipitate subsides, which was long regarded as a distinct oxide of chromium; but Thomson has proved that it is the green oxide combined with a little chromic acid. The acid may in a great measure be washed away by means of water, and by ammonia it is entirely removed; but the best mode of separating it is to dissolve the brown matter with hydrochloric acid, and then precipitate the green oxide by ammonia. The brown compound may be formed by boiling a solution of bichromate of potassa with alcohol; and it is also rapidly generated, when bichromate of potassa is gently boiled with sugar and a very little hydrochloric acid. The brown oxide, when pure, has the composition CrO_2, which is that of a binoxide; but it is now believed to be a compound of 1 eq. sesquioxide and 1 eq. chromic acid, $Cr_2O_3 + CrO_3 = Cr_3O_6$, which gives the same composition as CrO_2.

Its eq. is 52; symb. $Cr + 3O$, $\overset{\cdots}{Cr}$, or CrO_3.

According to Barreswill, there exists a perchromic acid, CrO_7, corresponding to permanganic acid. It is formed by the action of peroxide of hydrogen on chromic acid, and has a fine deep blue colour. It is almost immediately resolved, however, into chromic acid and oxygen.

Nituret of Chromium.—When ammonia is passed over sesquichloride of chromium heated in a tube, there is obtained a brown powder; and when the compound of oxychloride of chromium with ammonia is acted on by ammonia in the same way there is formed a black powder, which appears to be essentially the same. This compound was formerly described as metallic chromium, but Schrötter has shewn that it is a nituret of chromium. It burns, when heated in oxygen, with a red light, yielding sesquioxide of chromium and nitrogen gas.

In its formation sal ammoniac is produced, and hydrogen disengaged, as shewn by the equation $3(Cr_2Cl_3) + 13NH_3 = 2Cr_3N_2 + 9(NH_3,HCl) + H_3$.

Its eq. is 112; symb. $3Cr + 2N$, or Cr_3N_2.

Protochloride of Chromium.—Discovered by Peligot. Prepared by passing hydrogen over the sesquichloride at a temperature below that which softens glass. It is a white substance, which appears as a network, apparently of small crystals. It dissolves in water with disengagement of heat, and forms a blue solution, which contains a compound of 2 eq. protochloride and 1 eq. oxygen, hydrogen being given off. Its eq. is 63·42; symb. Cr + Cl, or CrCl.

Peligot has observed that it possesses a singular power of causing the sesquichloride, which, according to him, is quite insoluble in water, to dissolve in that fluid. Water containing only $\frac{1}{10,000}$th part of protochloride dissolves the sesquichloride.

Sesquichloride of Chromium.—It is prepared by transmitting dry chlorine gas over a mixture of oxide of chromium and charcoal heated to redness in a tube of porcelain, when the sesquichloride gradually collects as a crystalline sublimate of a peach-purple colour, which in thin layers is transparent, but in thicker masses is opaque. Another method is to evaporate the solution of the green oxide in hydrochloric acid gently to dryness at a temperature of 212°, when a green powder remains, consisting of 1 eq. of the sesquichloride and 3 eq. of water ($Cr_2Cl_3 + 3HO$), these elements being exactly in the ratio to form oxide of chromium and hydrochloric acid. On raising the temperature above 212°, no water is lost until it reaches 400°: the powder then begins to swell up from the escape of water, the colour changes from green to the red of peach-blossoms, and pure sesquichloride remains. This part of the process should be conducted in a tube from which air is excluded by a current of dry carbonic acid gas. These phenomena are justly quoted by Liebig as favouring the notion that the green solution and powder are a hydrochlorate of an oxide, and not a chloride with water; for Gregory has shewn (Journ. de Pharm.) that the pink powder, first obtained by Kemp from the action of chloride of sulphur on oxychloride of chromium, is nothing but pure sesquichloride. It is not crystalline, and quite insoluble in water; but by long exposure to air it appears to pass slowly into the soluble state. Being formed at a high temperature, it was supposed to differ from the soluble variety, as ignited alumina, peroxide of iron, or sesquioxide of chromium do from the same oxides previous to ignition. The insolubility of the chloride has lately been confirmed by Rose. (Annalen der Pharm. 1840.)

The sesquichloride of chromium is said by some chemists to dissolve slowly, forming a deep green solution. But Peligot has shewn this solubility is owing to the presence of the protochloride, which generally accompanies the sesquichloride, and that the pure chloride, as above stated, is quite insoluble. The same solution may be prepared by directly dissolving the hydrated oxide in hydrochloric acid; or by digesting chromate of oxide of lead in strong hydrochloric acid, adding a little alcohol from time to time to promote the deoxidation of chromic acid, and then separating the resulting chloride of chromium from that of lead by strong alcohol, which together with any excess of hydrochloric acid is ultimately expelled by evaporating to dryness. Traces of lead which may have been dissolved are easily precipitated by hydrosulphuric acid.

Its eq. is 162·26; symb. $2Cr + 3Cl$, or Cr_2Cl_3.

Sesquifluoride of Chromium is formed by dissolving the oxide in hydrofluoric acid, and evaporating the solution to dryness, when the sesquifluoride remains as a green crystalline residue, which is soluble in water. Its eq. is 112·04; symb. $2Cr + 3F$, or Cr_2F_3.

Perfluoride of Chromium.—Discovered by Unverdorben in 1825. (Ed. Journ. of Science, iv. 129.) When a mixture of 3 parts of fluor-spar and 4 of chromate of oxide of lead is distilled with 5 parts of fuming or even common sulphuric acid in a leaden or silver retort, a red-coloured gas is disengaged, which acts rapidly upon glass, with deposition of chromic acid and formation of fluosilicic acid gas. It is decomposed by water, and the solution is found to contain a mixture of hydrofluoric and chromic acids. The watery vapour of the atmosphere effects its decomposition, so that when mixed with air, red fumes appear, owing to the separation of minute crystals of chromic acid.

The red colour of terfluoride of chromium naturally excites the suspicion that the gas itself may consist, not of fluoride of chromium, but of hydrofluoric and chromic acids; and its production by means of *hydrous* sulphuric acid is consistent with this idea. But since the gas may also be formed from fluor-spar, chromate of oxide of lead, and *anhydrous* sulphuric acid, it is clear that this view is inadmissible. It was formerly considered to be composed of 1 eq. of chromium and 3 eq. of fluorine, and was hence described as the terfluoride. H. Rose has shewn, however, that its elements approximate more closely to the ratio of 1 to 5 rather than of 1 to 3; but its true constitution is not yet satisfactorily determined. It is perhaps CrF_5.

Sulphuret of Chromium may be formed by transmitting the vapour of bisulphuret of carbon over oxide of chromium at a white heat; by heating in close vessels an intimate mixture of sulphur and the hydrated oxide; by fusing the oxide with a persulphuret of potassium, and dissolving the soluble parts in water; or by transmitting hydrosulphuric acid gas aided by heat over the sesquichloride of chromium. It cannot be prepared in the moist way. It is of a dark grey colour, and acquires metallic lustre by friction in a mortar. It is readily oxidized when heated in the open air, and is dissolved by nitric or nitro-hydrochloric acid.

Its eq. is 104·3; symb. $2Cr + 3S$, or Cr_2S_3.

Phosphuret of Chromium.—Rose prepared this compound by acting on the sesquichloride of chromium by phosphuretted hydrogen gas at a red heat. By mutual interchange of elements,

1 eq. Sesquichloride	Cr_2Cl_3	yield	1 eq. Phosphuret	Cr_2P.
and 1 eq. Phosphur. Hyd.	PH_3		and 3 eq. Hydrochloric Acid	$3HCl$.

This phosphuret is black, insoluble in hydrochloric acid, feebly attacked by nitric and nitro-hydrochloric acid, and burns before the blowpipe with a flame of phosphorus.

Its eq. is 43·7; symb. $2\,Cr + P$, or Cr_2P.

Another phosphuret of a grey colour may be formed by exposing the phosphate of oxide of chromium to a strong heat in a covered crucible lined with charcoal. Its composition is unknown.

Oxychloride of Chromium.—*Hist.*—Discovered by Unverdorben at the same time as the perfluoride of chromium: it was long considered and described as the terchloride, until Rose pointed out its real constitution. (Pog. An. xxvii. 525.)

Prep.—By the action of fuming sulphuric acid on a mixture of about equal weights of chromate of oxide of lead and chloride of sodium. Wöhler recommends the following process:—10 parts of chloride of sodium are fused in a common crucible with 16·9 parts of the neutral chromate of potassa, the fused salts are thrown upon a clean stone, and the mass when cold is broken into coarse fragments. These are to be introduced into a capacious tubulated retort, to which a receiver kept cold by moistened paper is adapted. Twelve parts of fuming sulphuric acid are then added to the fused salts, when an energetic action commences, and in a few minutes the oxychloride is formed and distilled over without the application of external heat. (Pog. An. xxxiii. 343.)

Prop.—It is a heavy red liquid, exceedingly volatile, yielding abundant red vapours when exposed to the air. By water it is instantly decomposed into hydrochloric and chromic acids. Its vapour is decomposed by a red heat into oxide of chromium, oxygen, and chlorine, as observed by Wöhler, who has thus confirmed the composition of the oxychloride, as stated by Rose. The latter chemist found it was composed of 2 eq. of chromic acid and 1 eq. of a perchloride; and the former, that 2 eq. of the oxychloride produced 3 eq. of the oxide of chromium, 3 eq. of oxygen, and 6 eq. of chlorine. In symbols,

$$2\,(CrCl_3 + 2CrO_3) \quad \text{yield} \quad \begin{cases} 3Cr_2O_3. \\ 3O. \\ 6Cl. \end{cases}$$

Its eq. is 210·26; symb. $CrCl_3 + 2CrO_3$.

Millon considers it as chromic acid in which 1 eq. oxygen is replaced by chlorine, $Cr\left.\begin{matrix}Cl\\O_2\end{matrix}\right\}$. The same ingenious chemist has extended this view to the bleaching compounds of chlorine. Thus, bleaching powder, commonly viewed as $CaO,ClO + CaCl$, may be viewed as an oxychloride of calcium, $Ca\left.\begin{matrix}Cl\\O\end{matrix}\right\}$. For further details, I must refer to the foreign journals.

VANADIUM.

Hist.—Vanadium, so called from *Vanadis*, the name of a Scandinavian deity, was discovered in the year 1830 by Sefström, of Fahlun, in iron prepared from the iron-ore of Taberg in Sweden. The state in which it occurs in the ore is unknown; but Sefström separated it from the iron by dissolving the latter in hydrochloric acid, when a black powder came into view containing a small quantity of vanadium, together with iron, copper, cobalt, silex, alumina, and lime. He afterwards found a more abundant source in the slag or cinder formed during the conversion of the cast iron of Taberg into malleable iron. Soon after Sefström's discovery, the same metal was formed by Johnston, of Durham, in a mineral from Wanlockhead in Scotland, where it occurs as a vanadiate of oxide of lead. A similar mineral, found at Zimapan in Mexico, was examined in the year 1801 by Professor del Rio, who, in the belief of having discovered a new metal, gave it the name of *Erythronium*, apparently from the red colour of its acid; but as Collet Descotils, on being appealed to, declared the mineral to be chromate of lead, Del Rio abandoned his own opinion in deference to a higher authority. Thus have three persons noticed the existence of vanadium, without the knowledge of each other's labours; but the merit of being the first discoverer is fairly due to Sefström.* Wöhler has recently observed that some specimens of pitchblende, the ore of uranium, contain vanadium in small proportion. Schafhaütl has also discovered a variety of bronzite, containing 3·5 per cent. of vanadic acid; and the vanadiate of copper has been found in small quantity.

Prep.—From the slag above mentioned vanadic acid may be obtained by the following process, contrived by Sefström and improved by Berzelius:—The slag in fine powder, mixed with its own weight of nitre and twice its weight of carbonate of potassa, is strongly ignited for the space of one hour. The soluble parts are then removed by boiling water, and the solution, after being filtered and neutralized with colourless nitric acid, is precipitated by chloride of barium or acetate of lead. The precipitate, which consists of vanadiate and phosphate of baryta or oxide of lead, zirconia, alumina, and silicic acid, is decomposed, while still moist, by digestion with strong sulphuric acid; to the deep-red solution alcohol is then added, when by continued digestion ether is disengaged, and all the vanadic acid converted into the salifiable oxide, the solutions of which are blue,—a change effected in order the more completely to remove the vanadic acid from the insoluble matters. The blue liquid is then evaporated; and when it acquires a syrupy consistence, it is mixed in a platinum crucible with a little hydrofluoric acid, and sharply heated in an open fire. By this means the silicic acid, which can only be got rid of in this way, is converted into the gaseous fluoride of silicon, the sulphuric acid expelled, and the oxide reconverted into the acid of vanadium.

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* Phil. Mag. and Annals, x. 321. An. de Ch. et Ph. xlvii. 337. Brewster's Journal, v. 318, N. S. Poggendorff's Annalen, xxii. i.

The vanadic acid still contains phosphoric acid, alumina, and zirconia. For its further purification it is fused with nitre added in successive small portions, until, on cooling a small quantity, the red tint is found to have disappeared. In this process the acid of the nitre is displaced by the phosphoric and vanadic acids, the object being to cause those acids to unite with potassa without employing an excess of nitre. The vanadiate and phosphate of potassa are then taken up by as small a quantity of water as will suffice, and into the filtered liquid a piece of sal-ammoniac, larger than can be dissolved by it, is introduced: as it dissolves, vanadiate of ammonia, insoluble in a saturated solution of sal-ammoniac, subsides as a white powder, leaving the phosphoric acid in the liquid. The vanadiate of ammonia should be first washed with a solution of sal-ammoniac, and then with alcohol of sp. gr. 0·86.

By heating this salt in an open platinum crucible, vanadic acid is obtained; but the temperature ought to be kept below that of redness, and the mass be well stirred until it acquires a dark red colour. Heated in close vessels the vanadiate of ammonia is converted principally into the salifiable oxide; though some of the protoxide and acid are mixed with it. With the zirconia and alumina, left by the water after fusion with nitre, some vanadium remains: it may be extracted by fusion with sulphur and carbonate of potassa, when a double sulphuret of vanadium and potassium is generated, which is soluble in water. On adding sulphuric acid to the solution, sulphuret of vanadium is precipitated.

The preparation of vanadium from the native vanadiate of lead is much less complicated than the process above described. It suffices to dissolve the ore, as Johnston advises, in nitric acid, and to precipitate the lead by hydrosulphuric acid, which also throws down any arsenic that may be present. As vanadic acid is deoxidized by hydrosulphuric acid, a blue solution is formed; but by evaporating to dryness the acid is reproduced. The residue is then dissolved by a solution of ammonia, and the vanadiate of ammonia precipitated as before by a piece of sal-ammoniac. The vanadic acid is thus separated from arsenic, phosphoric, and hydrochloric acids, with which in the ore of Wanlockhead it is generally associated.

The attempts of Berzelius to reduce vanadic acid to the metallic state by the agency of hydrogen or charcoal at high temperatures proved unsuccessful, as the protoxide alone was obtained. He procured the metal, however, in the form of a heavy black powder, by placing fragments of fused vanadic acid and potassium of equal size in alternate layers in a porcelain crucible, the potassium being in the largest proportion: a cover was then luted on, and heat applied by means of a spirit-lamp. The reduction took place suddenly and with violence; and when the mass had cooled, the potassa and redundant potassium were separated by water. But Berzelius succeeded better by a process similar to that of H. Rose for procuring metallic titanium. The liquid chloride of vanadium is introduced into a glass bulb blown in a barometer tube, and through it is transmitted dry ammoniacal gas until a white saline mass is produced, during the formation of which the gas is rapidly absorbed, and heat disengaged. A spirit-lamp flame is then applied, which expels a quantity of hydrochlorate of ammonia, and metallic vanadium is left adhering to the interior of the bulb. The production of hydrochloric acid is obviously owing to chlorine leaving the vanadium and uniting with the hydrogen of part of the ammonia.

Prop.—The pulverulent vanadium, produced by means of potassium, has but little of the tenacity and appearance of a metal, though under strong pressure it assumes a lustre like that of graphite. Heated in the open air to commencing redness it takes fire, and is converted into the black protoxide. It conducts electricity, however, and is strongly electro-negative in relation to zinc. As procured by Rose's process the vanadium has a strong metallic lustre and a white colour considerably resembling silver, but still more like molybdenum. It is so extremely brittle that it cannot be removed from the glass bulb without falling into powder. It is not oxidized either by air or water; although by continued exposure to the air its lustre gradually grows weaker, and it acquires a reddish tint. It is not dissolved by boiling sulphuric, hydrochloric, or hydrofluoric acid; but by nitric and nitro-hydrochloric acid it is attacked, and the solution has a beautiful dark blue colour. It is not oxidized by being boiled with caustic potash, nor by carbonated alkalies at a red heat.

The eq. of vanadium, according to the analysis of its oxides by Berzelius, is 68·5; its symb. is V; and its compounds described in this section are thus constituted:—

	Vanadium.			Equiv.	Formulæ.
Protoxide .	68·5	1 eq.+Oxygen	8	1 eq.= 76·5	$V+O$ or Vo.
Binoxide .	68·5	1 eq.+ do.	16	2 eq.= 84·5	$V+2O$ or VO_2.
Vanadic Acid	68·5	1 eq.+ do.	24	3 eq.= 92·5	$V+3O$ or VO_3.
Bichloride .	68·5	1 eq.+Chlorine	70·84	2 eq.=139·34	$V+2Cl$ or VCl_2.
Terchloride .	68·5	1 eq.+ do.	106·26	3 eq.=174·76	$V+3Cl$ or VCl_3.
Bibromide .	68·5	1 eq.+Bromine	156·8	2 eq.=225·3	$V+2Br$ or VBr_2.
Bisulphuret .	68·5	1 eq.+Sulphur	32·2	2 eq.=100·7	$V+2S$ or VS_2.
Tersulphuret	68·5	1 eq.+ do.	48·3	3 eq.=116·8	$V+3S$ or VS_3.

Protoxide.—This compound is readily formed from vanadic acid, by the combined agency of heat and charcoal or hydrogen gas. By means of the latter Berzelius found that the reduction is effected as perfectly at a temperature short of ignition, as at the strongest heat of a wind furnace. When prepared from fused vanadic acid, the protoxide retains the crystalline structure of the acid, and has a black colour and a semi-metallic lustre; but it is easily broken down into a fine black powder. When rendered coherent by compression it possesses a property very unusual in oxides, that of conducting electricity, and in relation to zinc of being as strongly electro-negative as silver or copper.

It is very infusible. When heated in open vessels it takes fire and burns like tinder, being converted into the binoxide. On exposure to air and moisture it is slowly oxidized, a process which is best seen by putting it into water, when the liquid gradually acquires a green tint. In both cases the oxygen is derived from the atmosphere. A similar change occurs in acid and alkaline solutions, which, with the exception of nitric acid, do not dissolve it even at a boiling temperature. Heated in nitric acid oxidation ensues with escape of nitric oxide gas, and a blue nitrate of the binoxide of vanadium is generated. The character of an alkaline base seems wholly wanting in the protoxide, and hence Berzelius considers it as a *sub-oxide*.

Its eq. is 76·5; symb. $V + O$, $\dot{V}$, or VO.

Binoxide.—*Prep.*—Best prepared, in the dry way, by heating to full redness an intimate mixture of 10 parts of the protoxide with 12 of vanadic acid in a vessel filled with carbonic acid, or from which combustible matter on the one hand, and oxygen gas on the other, are carefully excluded. From the salts of the binoxide, and especially the sulphate, it is precipitated as a greyish-white hydrate by means of a very slight excess of carbonate of soda. The residual solution is colourless when the process has been properly conducted: it remains blue, from undecomposed salt, if an insufficient quantity of alkali is used; it is brown when the alkaline carbonate is too freely employed, because some of the binoxide is then dissolved by the free alkali; and if the solution contained vanadic acid, its colour after precipitation is green. The presence of the latter is avoided by transmitting hydrosulphuric acid gas into the solution, whereby vanadic acid is effectually converted into the binoxide, but the redundant gas should be expelled by gentle heat before the oxide is precipitated. As the hydrate, while moist, readily absorbs oxygen, and hence acquires a tint of brown, it must be washed and dried without exposure to the air. When thus prepared it retains its grey tint. By exposure to heat in a vessel from which the air is excluded, it gives out water, and acquires all the characters of the oxide prepared in the dry way.

Prop.—A black pulverulent substance, very infusible, insoluble in water, and free from any acid or alkaline reaction. When heated in the open air it is converted into vanadic acid, and when moist it gradually suffers the same change at ordinary temperatures. It is dissolved by acids more readily as a hydrate than after being heated to redness, and forms salts, most of which have a blue colour, and are more or less soluble in water. They may all be conveniently formed by the direct action of acids on the hydrated oxide. The nitrate may be made by acting on vanadium, or either of its oxides, by nitric acid; the salt, when diluted with water, may be boiled without change; but when evaporated, even spontaneously, the blue colour passes through green into red, owing to the production of vanadic acid. The sulphate is easily prepared by dissolving vanadic acid in warm sulphuric acid diluted with an equal weight of water, decomposing the vanadic acid by hydrosulphuric acid, concentrating the solution in order that the salt may be deposited, and washing away adhering sulphuric acid by means of alcohol. The deoxidation of vanadic acid in the preceding process may also be effected by adding pure oxalic acid as long as carbonic acid gas is evolved.

The salts of the binoxide of vanadium are distinguished by their blue colour, by yielding with the alkalies or their carbonates in very slight excess the hydrated binoxide, which becomes red by oxidation, and by forming with solution of gall-nuts a black compound, a tannate of the binoxide, very similar to ink.

The binoxide is disposed to act the part of an acid by uniting with alkaline bases, with which it forms definite, and in some cases crystalline, compounds. On digesting the hydrated binoxide in pure potassa or ammonia, combination is readily effected, and a dark brown solution is formed. These compounds, though soluble in water, are very sparingly so in strong and cold alkaline solutions, and may be precipitated by them. Most of the other salts formed by the binoxide and salifiable bases are insoluble in water, and may be formed from the preceding by way of double decomposition.

Its eq. is 84·5 ; symb. $V + 2O$, $\ddot{V}$, or VO_2.

Vanadic Acid.—When vanadiate of ammonia, prepared as already mentioned, is heated in close vessels, the acid is decomposed by the hydrogen of the ammonia, and binoxide of vanadium is formed, mixed with a little protoxide and undecomposed acid. If the salt is heated in an open vessel, and well stirred, the whole mass acquires a dark red colour, and pure vanadic acid is obtained: but a red heat should be avoided, since fusion would thereby be occasioned, and free exposure of every part to the atmosphere prevented. Its colour in the state of fine powder is a light rust-yellow; but the fused acid is red with a shade of orange, and has a strong lustre. By light transmitted through thin layers it appears yellow. In the fire it is fixed, and is not decomposed by very strong heat, provided combustible matters are excluded. It fuses at a heat lower than that of redness, and crystallizes readily as it cools. In the act of becoming solid it contracts considerably in volume, and emits so much heat of fluidity that the acid, after ceasing to be luminous, is again rendered incandescent, and remains so until the congelation is complete.

It is tasteless, insoluble in alcohol, and very slightly soluble in water, which takes up rather less than 1-100th of its weight, acquiring a yellow colour and an acid reaction. Heated with combustible matter it is deoxidized, being converted into the protoxide or binoxide, or mixtures of these oxides. In solutions it is deprived of oxygen by all deoxidizing agents, such as alcohol, sugar, and most organic substances, including the oxalic and several vegetable acids, by hydrosulphuric acid and most other of the hydracids, not excepting the hydrochloric, by sulphurous and phosphorous acids, and even by nitrous acid. Like molybdic and tungstic acids it is disposed to act as a base to such of the stronger acids as do not decompose it, and to form with them definite compounds, which are soluble in water. It unites on this principle with sulphuric and phosphoric acid; and Berzelius has remarked a compound of the phosphoric, silicic, and vanadic acids, a sort of double salt, in which the latter acid is a base to the two former, and which crystallizes in scales; it is formed in Sefström's process for preparing vanadic acid, and its solubility opposes a great obstacle to the separation of vanadic from silicic acid.

Vanadic acid unites with salifiable bases often in two or more proportions, forming soluble salts with the alkalies, and in general sparingly soluble salts with the other metallic oxides. Those with excess of acid are commonly of a red or orange-red colour. Most of the neutral salts are yellow; but it is singular that the neutral vanadiates of the alkalies, the alkaline earths, and the oxides of lead, zinc, and cadmium may be yellow at one time and colourless at another, without suffering any appreciable change in composition. Thus, on neutralizing vanadic acid with ammonia a yellow salt is obtained, the solution of which gradually becomes colourless if kept for some hours, and suffers the same change rapidly when heated. The solution, as it is coloured or colourless, gives a yellow or white residue by evaporation, and a yellow or white precipitate with a salt of baryta or oxide of lead. These changes may possibly be of the same kind as those already noticed in the description of phosphoric acid.

Vanadic acid unites in different proportions with binoxide of vanadium, and forms compounds which are soluble in pure water, but sparingly so in saline solutions, and which are purple, green, yellow, or orange, according as the acid is in a smaller or larger proportion. They are best formed by exposing the hydrated binoxide to the atmosphere, when these different colours successively appear, as a gradually increasing quantity of the acid is generated.

Vanadic acid is distinguished from all other acids except the chromic by its colour, and from this acid by the action of deoxidizing substances, which give a blue solution with the former and a green with the latter. When heated with borax in the reducing flame of the blowpipe, both of the acids yield a green glass; but in the oxidizing flame the bead becomes yellow if vanadium is present, while the green colour produced by chromium is permanent.

Its eq. is 92·5; symb. $V + 3O$, $\dddot{V}$, or VO_3.

Chlorides.—The bichloride is prepared by digesting a mixture of the vanadic and hydrochloric acids, deoxidizing any undecomposed vanadic acid by hydrosulphuric acid, and evaporating the solution to dryness. A brown residue is obtained, which yields a blue solution with water, part being left as an insoluble sub-salt. It may also be generated by acting directly on the ignited binoxide with strong hydrochloric acid. As thus obtained its solution is brown instead of blue, though in composition it seems identical with the preceding.

Its eq. is 139·34; symb. $V + 2Cl$, or VCl_2.

The *terchloride* may be formed by transmitting a current of dry chlorine gas over a mixture of protoxide of vanadium and charcoal heated to a low redness, when the terchloride passes over in vapour, and condenses in the form of a yellow liquid, from which free chlorine may be removed by a current of dry air. It is converted by water into hydrochloric and vanadic acid, and atmospheric humidity produces the same change, which is indicated by the escape of red fumes.

Its eq. is 174·76; symb. $V+3Cl$, or VCl_3.

A *bibromide* of vanadium may be formed in the same manner as the bichloride, substituting the hydrobromic for hydrochloric acid. Similar compounds may be procured with iodine, fluorine, and cyanogen, by dissolving binoxide of vanadium in hydriodic, hydrofluoric, and hydrocyanic acids.

Sulphurets.—When the binoxide of vanadium is heated to redness in a current of hydrosulphuric acid gas, it is converted into protoxide, and both water and sulphur are obtained: on continuing the process, the protoxide is decomposed, hydrogen gas and water pass over, and bisulphuret of vanadium is generated. This compound may also be procured by mixing hydrosulphate of ammonia with a salt of the binoxide of vanadium until the precipitate at first formed is redissolved, and then decomposing the deep purple-coloured solution by sulphuric or hydrochloric acid. The bisulphuret of a brown colour subsides, which becomes black when it is dried. It is unchanged at common temperatures by exposure to the air, but takes fire when heated. In the hydrated state it is dissolved by alkalies and alkaline sulphurets; but it is insoluble in acids, with the exception of the nitric and nitrohydrochloric, by which it is converted into sulphate of the binoxide.

Its eq. is 100·7; symb. $V+2S$, or VS_2.

When hydrosulphuric acid gas is transmitted through an aqueous solution of vanadic acid, a greyish-brown precipitate is formed, consisting of hydrated binoxide of vanadium mixed mechanically with sulphur. But if a solution of vanadic acid in hydrosulphate of ammonia is acidulated by hydrochloric or sulphuric acid, the hydrated *tersulphuret* of vanadium subsides. Its colour is of a much lighter brown than the bisulphuret, becomes almost black in drying, and is resolved by a red heat in close vessels into the bisulphuret with loss of water and sulphur. It is soluble in alkalies and alkaline sulphurets, and is oxidized by nitric acid.

Its eq. is 116·8; symb. $V+3S$, or VS_3.

The phosphuret of vanadium, of a leaden-grey colour, may be formed by exposing to a white heat phosphate of the binoxide of vanadium mixed with a small quantity of sugar.

SECTION XVII.

MOLYBDENUM.—TUNGSTEN.—COLUMBIUM.

MOLYBDENUM.

Hist. and Prep.—The principal ore of molybdenum is the sulphuret, which was long mistaken for graphite, and was first distinguished from it in 1778 by Scheele; but the metal was obtained in a separate state by Hjelm. When this ore, in fine powder, is digested in nitro-hydrochloric acid until it is completely decomposed, and the residue is briskly heated in order to expel sulphuric acid, molybdic acid remains in the form of a white heavy powder. From this acid metallic molybdenum may be obtained by exposing it with charcoal to the strongest heat of a smith's forge; or by conducting over it a current of hydrogen gas while strongly heated in a tube of porcelain. (Berzelius.) Molybdenum likewise occurs in nature in the form of molybdate of oxide of lead.

Prop.—It is a brittle metal, of a white colour, and so very infusible, that hitherto it has only been obtained in a state of semifusion. In this form it has a sp. gr. varying between 8·615 and 8.636. When heated in open vessels, it absorbs oxygen, and is converted into *molybdic acid;* and the same compound is generated by the action of chlorine or nitro-hydrochloric acid. It has three degrees of oxidation, forming two oxides and one acid, from the composition of which Berzelius estimates the eq. of molybdenum at 47·7. Its symb. is Mo. The composition of its compounds described in this section is as follows:—

	Molybdenum.				Equiv.	Formulæ.
Protoxide .	47·7	1 eq.+Oxygen	8	1 eq.=	55·7	$Mo+O$ or MoO.
Binoxide .	47·7	1 eq.+ do.	16	2 eq.=	63·7	$Mo+2O$ or MoO_2.
Molybdic Acid .	47·7	1 eq.+ do.	24	3 eq.=	71·7	$Mo+3O$ or MoO_3.
Protochloride .	47·7	1 eq.+Chlorine	35·42	1 eq.=	83·12	$Mo+Cl$ or $MoCl$.
Bichloride .	47·7	1 eq.+ do.	70·84	2 eq.=	118·54	$Mo+2Cl$ or $MoCl_2$.
Bisulphuret .	47·7	1 eq.+Sulphur	32·2	2 eq.=	79·9	$Mo+2S$ or MoS_2.
Tersulphuret .	47·7	1 eq.+ do.	48·3	3 eq.=	96·0	$Mo+3S$ or MoS_3.
Persulphuret .	47·7	1 eq.+ do.	64·4	4 eq.=	112·1	$Mo+4S$ or MoS_4.
Oxychloride MoO_3	143·4	2 eq.+$MoCl_3$	153·96	1 eq.=	297·36	$2MoO_3+MOCl_3$.

Protoxide of Molybdenum.—On dissolving molybdate of potassa or soda in a small quantity of water, adding hydrochloric acid until the molybdic acid at first thrown down is redissolved, and digesting with a piece of pure metallic zinc, the latter deoxidizes the molybdic acid, the liquid changes to blue, red, and black, and then contains chloride of zinc and protochloride of molybdenum. From the black solution pure potassa throws down the protoxide of molybdenum as a black hydrate, an excess of the alkali being used in order to hold the zinc in solution. The hydrate is washed with the least possible exposure to the air, and dried in vacuo by sulphuric acid. When heated to low redness in the open air it takes fire and is converted into the binoxide; but if not exposed to the air it becomes incandescent at the moment of losing its water, like hydrated oxide of chromium. The anhydrous oxide is black and insoluble in acids; but in the state of hydrate, acids dissolve it. The recently precipitated hydrate is soluble in the cold by carbonate of ammonia, but in none of the other alkalies.

Its eq. is 55·7; symb. $Mo + O$, $\dot{Mo}$, or MoO.

Binoxide of Molybdenum.—Prep.—Obtained as a deep brown anhydrous powder by mixing molybdate of soda with half its weight of sal-ammoniac in fine powder, projecting the mixture into a red-hot crucible, which is to be instantly covered, and the heat continued until vapours of sal-ammoniac cease to appear. In this process chloride of sodium is generated, and molybdic acid is reduced by the ammonia to the state of binoxide: by adding water to the mass when cold chloride of sodium is dissolved, and the dark brown, nearly black, binoxide left. The hydrate, of a rust-brown colour, may be formed by digesting molybdenum in powder with molybdic acid dissolved in hydrochloric acid, until the liquid acquires a deep red colour, and then adding ammonia; or by adding ammonia to a solution of the bichloride; or digesting with metallic copper a solution of molybdic in hydrochloric acid until a deep red solution is formed, and employing an excess of ammonia in order to keep oxide of copper in solution.

Prop.—The anhydrous binoxide is insoluble in acids and is changed into molybdic acid by strong nitric acid. The hydrate is very like hydrated peroxide of iron, reddens litmus paper when placed on it, is dissolved by acids with which it forms red salts, is insoluble in the alkalies, but dissolves in alkaline carbonates. It is soluble, though sparingly, in pure water, so that it should be washed after precipitation by a solution of sal-ammoniac, which salt is afterwards removed by alcohol. On exposure to the air, the hydrate absorbs oxygen and becomes blue at its surface: this blue compound is more soluble in water than the hydrate, and was supposed by Bucholz to be a distinct acid, which he termed *molybdous acid;* but Berzelius has shewn that it is a bimolybdate of the binoxide. (Berzelius.)

Its eq. is 63·7; symb. $Mo + 2O$, $\ddot{Mo}$, or MoO_2.

Molybdic Acid.—Prep.—When sulphuret of molybdenum is roasted in an open crucible kept at a low red heat, and constantly stirred, until sulphurous acid ceases to escape, a dirty yellow powder is left, which contains impure molybdic acid. The acid is taken up by ammonia and the filtered solution evaporated to dryness; it is again taken up by a little dilute ammonia and filtered; it is then purified by crystallization. On heating gently in an open platinum crucible, taking care to prevent fusion, the ammonia is expelled, and pure acid remains. It is also obtained by oxidizing the binoxide with nitric acid.

Prop.—As thus formed, it is a white powder, of sp. gr. 3·49, fusible by a red heat into a yellow liquid, which bears a strong red heat in closed vessels without subliming, but in an open crucible rises with the current of air, and collects on cold surfaces in colourless crystalline scales. It requires 570 times its weight of water for solution, which nevertheless has an acid reaction. It is soluble in the alkalies, forming colourless molybdates, from which molybdic acid is precipitated by the stronger acids, though an excess of the acids dissolves it; but after exposure to a red heat it is insoluble in acids.

Chlorides.—Berzelius has described three chlorides of molybdenum which he considered analogous in composition to the oxides; but his terchloride has recently been shown by Rose to be an oxychloride which has the same constitution as the oxychloride of chromium. (Pog. An. xl. 395.)

The protochloride is formed by dissolving the hydrated protoxide in hydrochloric acid, when it forms a deep nearly black coloured solution, which leaves a black viscid mass by evaporation.

Its eq. is 83·12; symb. $Mo + Cl$, or $MoCl$.

The *bichloride* is obtained as above mentioned, and yields a red solution. It is obtained in the anhydrous state by gently heating molybdenum in powder in dry chlorine gas, atmospheric air being excluded. The metal takes fire at its surface, but it is soon extinguished, after which the chlorine is replaced by a red vapour of such intensity that it is completely opaque in a vessel $\frac{3}{4}$ inch in diameter: this vapour condenses in the cooler parts of the apparatus in brilliant black crystals just like those of iodine, which are very fusible, and sublime at a gentle heat. Exposed to dry oxygen gas it is transformed gradually into oxychloride of molybdenum and molybdic acid. With water the bichloride acts violently from the intense heat evolved, and the whole is dissolved.

Its eq. is 118·54; symb. $Mo + 2Cl$, or $Mo\text{Ͼ}l_2$.

Sulphurets.—Molybdenum combines with sulphur in three proportions. The lowest grade is the *bisulphuret*, which is the most common ore of molybdenum, and is usually associated with ores of tin, has a lead-grey colour and metallic lustre resembling graphite, for which it was formerly mistaken. Its density varies from 4·138 to 4·569. It bears a strong heat in close vessels without change or fusion; but it is oxidized by nitric acid or by the joint action of heat and air.

Its eq. is 79·9; symb. Mo + 2S, or MoS_2.

The *tersulphuret* is obtained by saturating molybdate of potassa, soda, or ammonia with hydrosulphuric acid gas, and adding hydrochloric acid, when the tersulphuret falls of a deep brown colour, which becomes black on drying. It is partially oxidized when dried in the air. By heat in close vessels it is changed into the bisulphuret with loss of sulphur.

Its. eq. is 96; symb. Mo + 3S, or MoS_3.

The persulphuret is made by boiling the sulphur-salt formed of tersulphuret of molybdenum and sulphuret of potassium for a long time with the bisulphuret of molybdenum, when a precipitate collects which is to be well washed with cold water. It is a sulphur-salt composed of persulphuret of molybdenum and sulphuret of potassium, which forms with boiling water a deep red solution, from which on the addition of hydrochloric acid the persulphuret subsides.

Its eq. is 112·1; symb. MO + 4S, or MoS_3.

Oxychloride of Molybdenum.—Formerly described as a terchloride. It is obtained by heating the binoxide in a current of dry chlorine. It is white with a shade of yellow, sublimes at a heat short of redness, and condenses into crystalline scales. It dissolves in water, but the solution is slightly milky from the separation of molybdic acid. From its composition, which has been recently determined by Rose, it would appear that

3 eq. of Binoxide and	3 eq. of Chlorine	yield	1 eq. of Oxychloride
$3MoO_2$	$3Cl$.		$MoCl_3+2MoO_3$.

Its eq. is 297·36; symb. $MoCl_3+2MoO_3$.

TUNGSTEN.

It derives its name from the Swedish words *Tung Sten*, *heavy stone*, from the density of its ores; and it is called wolfram from the mineral of that name, which is a tungstate of the oxides of iron and manganese. This metal may be procured in the metallic state by exposing tungstic acid to the action of charcoal or dry hydrogen gas at a red heat; but though the reduction is easily effected, an exceedingly intense temperature is required for fusing the metal. Tungsten has a greyish-white colour, and considerable lustre. It is brittle, nearly as hard as steel, and less fusible than manganese. Its sp. gr. is near 17·4. When heated to redness in the open air it takes fire, and is converted into tungstic acid; and it undergoes the same change by the action of nitric acid. Digested with a concentrated solution of pure potash, it is dissolved with disengagement of hydrogen gas, and tungstate of potash is generated.

Chemists are acquainted with two compounds of this metal and oxygen; namely, the *dark brown oxide*, and the *yellow acid of tungsten;* and according to the analyses of Berzelius, (An. de Ch. et Ph. xvii.,) the oxygen of the former is to that of the latter in the ratio of two to three. From the composition of the latter, and assuming that it contains three atoms of oxygen, the eq. of tungsten is 99·7. Its symb. is W. Its compounds described in this section are thus constituted:—

	Tungsten.			Equiv.	Formulæ.
Binoxide .	99·7	1 eq.+Oxygen	16	2 eq.=115·7	$W+2O$ or WO_2.
Blue Oxide .	199·4	2 eq.+ do.	24	3 eq.=223·4	$2W+3O$ or W_2O_3.
Tungstic Acid .	99·7	1 eq.+ do.	24	3 eq.=123·7	$W+3O$ or WO_3.
Bichloride .	99·7	1 eq.+Chlorine	70·84	2 eq.=170·54	$W+2Cl$ or WCl_2.
Bisulphuret .	99·7	1 eq.+Sulphur	32·2	2 eq.=131·9	$W+2S$ or WS_2.
Persulphuret .	99·7	1 eq.+ do.	48·3	3 eq.=148·0	$W+3S$ or WS_3.
Oxychloride WO_3	257·4	2 eq.+WCl_3	205·96	1 eq.=463·36	$2WO_3+WCl_3$.

Binoxide.—Prep.—By the action of hydrogen gas on tungstic acid at a low red heat; but the best mode of procuring it, both pure and in quantity, is that recommended by Wöhler. (Quarterly Journal of Science, xx. 177.) This process consists in mixing wolfram in fine powder with twice its weight of carbonate of potassa, and fusing the mixture in a platinum crucible. The resulting tungstate of potassa is dissolved in hot water, mixed with about half its weight of hydrochlorate of ammonia in solution, evaporated to dryness, and exposed in a hessian crucible to a red heat. The mass is well washed with boiling water, and the insoluble matter digested in dilute potassa to remove any tungstic acid. The residue is oxide of tungsten. It appears that in this process the tungstate of potassa and hydrochlorate of ammonia mutually decompose each other, so that the dry mass consists of chloride of potassium and tungstate of ammonia. The elements of the latter react on each other at a red heat, giving rise to water, nitrogen gas, and oxide of tungsten; and this compound is protected from oxidation by the fused chloride of potassium with which it is enveloped. This oxide is also formed by putting tungstic acid in contact with zinc in dilute hydrochloric acid. The tungstic acid first becomes blue, and then assumes a copper colour; but the oxide in this state can with difficulty be preserved, as by exposure to the air, and even under the surface of water, it absorbs oxygen, and is reconverted into tungstic acid.

Prop.—When prepared by means of hydrogen gas, it has a brown colour, and when polished acquires the colour of copper; but when procured by Wöhler's process, it is nearly black. It does not unite, so far as is known, with acids; and when heated to near redness, it takes fire and yields tungstic acid.

Its eq. is 115·7; symb. $W + 2O$, $\ddot{W}$, or WO_2.

Tungstic Acid.—Prep.—Conveniently by digesting native tungstate of lime, very finely levigated, in nitric acid; by which means nitrate of lime is formed, and tungstic acid separated in the form of a yellow powder. Long digestion is required before all the lime is removed; but the process is facilitated by acting upon the mineral alternately by nitric acid and ammonia. The tungstic acid is dissolved readily by that alkali, and may be obtained in a separate state by heating the tungstate of ammonia to redness. Tungstic acid may also be prepared by the action of hydrochloric acid on wolfram. It is also obtained by heating the brown oxide to redness in open vessels.

Prop.—Tungstic acid is of a yellow colour, is insoluble in water, and has no action on litmus paper. With alkaline bases it forms salts called *tungstates*, which are decomposed by the stronger acids, the tungstic acid in general falling combined with the acid by which it is precipitated. When strongly heated in open vessels it acquires a green colour, and becomes blue when exposed to the action of hydrogen gas at a temperature of 500° or 600° F. The blue compound, according to Berzelius, is a tungstate of the oxide of tungsten; and the green colour is probably produced by an admixture of this compound with the yellow acid.

Its eq. is 123·7; symb. $W + 3O$, $\dddot{W}$, or WO_3.

Malaguti finds that the blue compound, formed in the manner stated above, is never constant in its composition; but he obtained a definite compound by heating tungstic acid by the flame of a spirit-lamp in a current of dry hydrogen. According to his analysis it contains 17·72 per cent. of oxygen; and he considers it a distinct acid, the constitution of which is represented by the symb. $2W + 5O$, or W_2O_5. (An de Ch. et Ph. lx. 271.)

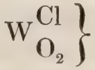
Chlorides of Tungsten.—Tungsten and chlorine unite in two proportions. When metallic tungsten is heated in chlorine gas, it takes fire and yields the bichloride. The compound appears in the form of delicate needles, resembling wool, of a deep red colour, but more frequently as a deep red fused mass, which has the brilliant fracture of cinnabar. When heated it fuses, boils, and yields a red vapour. By water it is changed into hydrochloric acid and oxide of tungsten. It is entirely dissolved by solution of pure potassa, with disengagement of hydrogen gas, yielding tungstate of potassa and chloride of potassium. A similar change is produced by ammonia, except that some oxide of tungsten is left undissolved.

Its eq. is 170·54; symb. $W + 2Cl$, or WCl_2.

Another chloride has been described by Wöhler. It is formed at the same time as the first; by the action of water it is converted into hydrochloric and tungstic acids. It is the most beautiful of all these compounds, existing in long transparent crystals of a fine red colour. It is very fusible and volatile, and its vapour is red like that of nitrous acid. The difference between this compound and the chloride first described is not yet satisfactorily determined; for although the analysis of Malaguti in his paper above referred to would indicate its constitution to be similar to that of his blue oxide, and therefore W_2Cl_5, still the errors into which he fell in reference to the terchloride throw suspicion on this result. The production of tungstic acid by its decomposition with water strengthens this suspicion.

Sulphurets of Tungsten.—The protosulphuret is obtained as a black powder by transmitting hydrosulphuric acid gas, or the vapour of sulphur, over tungstic acid heated to whiteness in a tube of porcelain. The persulphuret is prepared by dissolving tungstic acid in a solution of sulphuret of potassium or hydrosulphate of ammonia, and adding an excess of hydrosulphuric acid. It falls as a brown precipitate, which becomes black in drying. It is soluble to a certain extent in water which is free from saline matter.

Oxychloride of Tungsten.—Formerly described as the terchloride. It was discovered by Wöhler, and prepared by heating the binoxide of tungsten in a stream of dry chlorine gas. The action is attended with the appearance of combustion, dense fumes arise, and a thick sublimate is obtained in the form of scales, like native boracic acid. It is volatile at a low temperature without previous fusion. According to Rose, who has determined its composition, (Pog. An. xl. 395,) it is resolved when suddenly heated into tungstic acid, the bichloride of tungsten, and chlorine.

Its eq. is 463·36; symb. $WCl_3 + 2WO_3$; or, as in the case of the corresponding compound of chromium,  $W\begin{matrix}Cl\\O_2\end{matrix}\Big\}$.

COLUMBIUM.

Hist.—This metal was discovered in 1801 by Hatchett, who detected it in a black mineral belonging to the British Museum, supposed to have come from Massachusets, in North America; and from this circumstance applied to it the name of *columbium.* About two years after, M. Ekeberg, a Swedish chemist, extracted a substance from *tantalite* and *yttro-tantalite;* which, on the supposition of its being different from columbium, he described under the name of *tantalum.* The identity of these metals, however, was asserted in the year 1809 by Wollaston.

Prep.—Columbic acid is with difficulty reduced to the metallic state by the action of heat and charcoal; but Berzelius succeeded in obtaining this metal by the same process which he employed in the preparation of zirconium and silicon, namely, by heating potassium with the double fluoride of potassium and columbium. On washing the reduced mass with hot water, in order to remove the fluoride of potassium, columbium is left in the form of a black powder.

Prop.—As a powder it does not conduct electricity; but in a denser state it is a perfect conductor. By pressure it acquires metallic lustre, and has an iron-grey colour. It is not fusible at the temperature at which glass is fused. When heated in the open air it takes fire considerably below the temperature of ignition, and glows with a vivid light, yielding columbic acid. It is scarcely at all acted on by the sulphuric, hydrochloric, or nitro-hydrochloric acid; whereas it is dissolved with heat and disengagement of hydrogen gas by hydrofluoric acid, and still more easily by a mixture of nitric and hydrofluoric acids. It is also converted into columbic acid by fusion with hydrate of potassa, the hydrogen gas of the water being evolved.

From the experiments of Berzelius on the composition of the oxide and acid of columbium, its eq. may be estimated at 185. Its symb. is Ta. The compounds described in this section are thus constituted:—

	Columbium.				Equiv.	Formulæ.
Binoxide .	185	1 eq.+Oxygen	16	2 eq.=	201	Ta+2O or TaO_2.
Columbic Acid	185	1 eq.+ . .	24	3 eq.=	209	Ta+3O or TaO_3.
Terchloride .	185	1 eq.+Chlorine	106·26	3 eq.=	291·26	Ta+3Cl or $TaCl_3$.
Terfluoride .	185	1 eq.+Fluorine	56·04	3 eq.=	241·04	Ta+3F or TaF_3.
Sulphuret .	Composition uncertain.					

Oxide of Columbium.—It is generated by placing columbic acid in a crucible lined with charcoal, luting carefully to exclude atmospheric air, and exposing it for an hour and a half to intense heat. The acid, where in direct contact with charcoal, is entirely reduced; but the film of metal is very thin. The interior portions are pure oxide of a dark grey colour, very hard and coherent. When reduced to powder its colour is dark brown. It is not attacked by any acid, even by the nitro-hydrofluoric; but it is converted into columbic acid, either by fusion with hydrate of potassa or deflagration with nitre. When heated to low redness it takes fire and glows, yielding a light grey powder; but in this way it is never completely oxidized. Berzelius states that this oxide, in union with protoxide of iron and a little protoxide of manganese, occurs at Kimito in Finland, and may be distinguished from the other ores of columbium by yielding a chesnut-brown powder.

Its eq. is 201; symb. $Ta + 2O$, $\ddot{Ta}$, or TaO_2.

Columbic Acid.—Columbium exists in most of its ores as an acid, united either with the oxides of iron and manganese, as in tantalite, or with the earth yttria, as in the yttro-tantalite. This acid is obtained by fusing its ore with three or four times its weight of carbonate of potassa, when a soluble columbate of that alkali results, from which columbic acid is precipitated as a white hydrate by acids. Berzelius also prepares it by fusion with bisulphate of potassa.

Hydrated columbic acid is tasteless, and insoluble in water; but when placed on moistened litmus paper, it communicates a red tinge. It is dissolved by the sulphuric, hydrochloric, and some vegetable acids; but it does not diminish their acidity, or appear to form definite compounds with them. With alkalies it unites readily; and though it does not neutralize their properties completely, crystallized salts may be obtained by evaporation. When the hydrated acid is heated to redness, water is expelled, and the anhydrous columbic acid remains. In this state it is attacked by alkalies only.

Its eq. is 209; symb. $Ta + 3O$, $\dddot{Ta}$, or TaO_3.

Perchloride of Columbium.—When columbium is heated in chlorine gas, it takes fire and burns actively, yielding a yellow vapour, which condenses in the cold parts of the apparatus in the form of a white powder with a tint of yellow. Its texture is not in the least crystalline. By contact with water it is converted, with a hissing noise and increase of temperature, into columbic and hydrochloric acids. Hence its eq. is considered to be 291·26; symb. $Ta + 3Cl$, or $TaCl_3$.

Terfluoride of Columbium.—Hydrofluoric acid takes up hydrated columbic acid, and forms with it a compound of terfluoride of columbium and hydrofluoric acid, which, by evaporation at 76°, is deposited in crystals, which are soluble in water and effervesce in the air. By gently evaporating the solution, an uncrystalline mass, white and opaque, is left, which Berzelius considers to be the terfluoride of columbium. By water part of it is converted into columbic and hydrofluoric acids, the latter soluble and the former insoluble; but both of these acids retain some terfluoride in combination. Its eq. is 241·04; symb. $Ta + 3F$, or TaF_3.

Sulphuret of Columbium.—This compound, first prepared by Rose, is generated, with the phenomena of combustion, when columbium is heated to commencing redness in the vapour of sulphur; or by transmitting the vapour of bisulphuret of carbon over columbic acid in a porcelain tube at a white heat, carbonic oxide being also evolved.

NIOBIUM.

The above account of columbium or tantalum has not been altered; but the recent researches of H. Rose render it highly probable that the ores contain two analogous metals. One of these, when purified, retains the name of tantalum; and the other is called by Rose niobium, from Niobe, the daughter of Tantalus. The experiments of Rose not being finished, it is impossible to give an accurate account of both. The property observed in the tantalates of giving with hydrochloric acid and zinc a blue solution, appears to depend on the presence of niobium; and it was because this property was observed in the American mineral, and not in some of Ekeberg's tantalates, that Berzelius always denied the identity of columbium and tantalum. Rose finds niobium both in the Bavarian tantalates, and in the American columbite, and torrelite. The discovery of niobium will no doubt enable chemists to clear up the obscurities and contradictions connected with the subject. The discovery, in the same ores, of another metal, named pelopium, was announced by Rose about the same time with niobium; but I cannot find any account of it.

SECTION XVIII.

ANTIMONY.

Hist.—First made known as a metal in the 15th century by Basil Valentine, and is said to derive its name (*anti-moine*, *anti-monk*) from having proved fatal to some monks to whom it was given as a medicine. It sometimes occurs native; but its only ore, which is abundant, and from which the antimony of commerce is derived, is the sulphuret. This ore, the *stibium* of the ancients, was long regarded as the metal itself, and was called *antimony*, or *crude antimony;* while the pure metal was termed the *regulus* of *antimony*.

Prep.—Either by heating the native sulphuret, taking care to procure a sulphuret free from arsenic, in a covered crucible with half its weight of iron filings; or by mixing it with two-thirds of its weight of cream of tartar and one-third of nitre, and throwing the mixture, in small successive portions, into a red-hot crucible. By the first process the sulphur unites with iron, and in the second it is expelled in the form of sulphurous acid; while the fused antimony, which in both cases collects in the bottom of the crucible, may be drawn off and received in moulds. The antimony thus obtained is not absolutely pure; and therefore, for chemical purposes, should be procured by heating the oxide with an equal weight of cream of tartar. The antimony of commerce generally contains iron and arsenic. It may be purified by fusing 16 parts for an hour with 1 part of the sulphuret and 2 of dry carbonate of soda. The regulus thus obtained is to be fused again for an hour with 1½ parts of carbonate of soda; and this operation, if necessary, may be repeated with 1 part of the carbonate. In this way Liebig states that 15 parts of a perfectly pure regulus will be obtained. According to Berzelius, a trace of arsenic is still left.

Prop.—A brittle metal, of a white colour running into bluish-grey, and possessed of considerable lustre. Its sp. gr. is nearly 6·7. At 810° it fuses, and on cooling acquires a highly lamellated texture, and sometimes yields crystals: like arsenic, but unlike most other metals, its primary form is a rhombohedron. It is volatile at a very intense temperature. Its surface tarnishes by exposure to the atmosphere; and by the continued action of air and moisture a dark matter is formed, which Berzelius regards as a definite compound. It appears, however, to be merely a mixture of the teroxide and metallic antimony. Heated to a white or even full red heat in a covered crucible, and then suddenly exposed to the air, it inflames, and burns with a white light. During the combustion a white vapour rises, which condenses on cool surfaces, frequently in the form of small shining needles of silvery whiteness. These crystals were formerly called *argentine flowers of antimony*, and in chemical works are generally described as binoxide of antimony; but they are correctly considered by Berzelius as the teroxide. Antimony is an ingredient of various alloys, the most valuable of which is type metal.

From the experiments of Berzelius on the composition of the oxide and acids of antimony (An. de Ch. et Ph. xvii.), the eq. of that metal has been estimated at 64·6; but I prefer employing the double of that number, and thus, as in the cases of phosphorus and arsenic, getting rid of the complexity occasioned by assuming 2 eq. of the metal in all its compounds. The composition of its compounds described in this section is as follows:—

	1 eq. Antimony.			Equiv.	Formulæ.
Teroxide .	129·2+Oxygen	24	3 eq.	= 153·2	Sb+3O or SbO_3.
Antimonious Acid	129·2+ do.	32	4 eq.	= 161·2	Sb+4O or SbO_4.
Antimonic Acid .	129·2+ do.	40	5 eq.	= 169·2	Sb+5O or SbO_5.

	1 eq. Antimony.			Equiv.	Formulæ.
Terchloride .	129·2 + Chlorine	106·26	3 eq.	= 235·46	$Sb+3Cl$ or $SbCl_3$.
Quadrichloride .	129·2 + do.	141·68	4 eq.	= 270·88	$Sb+4Cl$ or $SbCl_4$.
Perchloride .	129·2 + do.	177·1	5 eq.	= 306·3	$Sb+5Cl$ or $SbCl_5$.
Bromide .	Composition uncertain.				
Tersulphuret .	129·2 + Sulphur	48·3	3 eq.	= 177·5	$Sb+3S$ or SbS_3.
Quadrisulphuret .	129·2 + do.	64·4	4 eq.	= 193·6	$Sb+4S$ or SbS_4.
Persulphuret .	129·2 + do.	80·5	5 eq.	= 209·7	$Sb+5S$ or SbS_5.
Oxychloride of Antimony .	Terchloride Teroxide	570·92 1378·8	2 eq. 9 eq.	=1949·72	$2SbCl_3+9SbO_3$.
Oxysulphuret of Antimony .	Tersulphuret Teroxide	355 153·2	2 eq. 1 eq.	= 508·2	SbS_3+SbO_3.

Teroxide.—*Syn. Sesquioxide.*—When terchloride of antimony, made by boiling the native sulphuret in hydrochloric acid, is poured into water, a white curdy precipitate subsides, formerly called *powder of Algaroth*, which consists of teroxide of antimony combined with undecomposed chloride. On decomposing the latter by digestion with carbonate of potassa, and then washing with water, the sesquioxide is obtained in a state of purity. It may also be procured by adding carbonate of potassa or soda to a solution of tartar emetic, and by sublimation during the combustion of antimony. When slowly sublimed it condenses in fine needles of silvery whiteness. It occurs as a mineral, the oxide of antimony of mineralogists, the primary form of which is a right rhombic prism, isomorphous with the crystals of arsenious acid lately observed by Wöhler.

Prop.—When prepared in the moist way, it is a white powder with a somewhat dirty appearance. When heated it acquires a yellow tint, and at a dull red heat in close vessels it is fused, yielding a yellow fluid, which becomes an opaque greyish crystalline mass on cooling. Its sp. gr. is 5·566. It is very volatile, and if protected from atmospheric air may be sublimed without change. When heated in open vessels it absorbs oxygen; and when the temperature is suddenly raised, and the oxide is porous, it takes fire and burns. In both cases antimonious acid is generated. It is the only oxide of antimony which forms regular salts with acids, and is the base of the medicinal preparation *tartar emetic*, the tartrate of antimony and potash. Most of its salts, however, are either insoluble in water, or, like chloride of antimony, are decomposed by it, owing to the affinity of that fluid for the acid being greater than that of the acid for oxide of antimony. This oxide is therefore a feeble base; and, indeed, possesses the property of uniting with alkalies. To the foregoing remark, however, tartrate of antimony and potassa is an exception; for it dissolves readily in water without change. By excess of tartaric or hydrochloric acid, the insoluble salts of antimony may be rendered soluble in water.

The presence of antimony in solution is easily detected by hydrosulphuric acid gas. This gas occasions an orange-coloured precipitate, hydrated tersulphuret of antimony, which is soluble in pure potassa, and is dissolved with disengagement of hydrosulphuric acid gas by hot hydrochloric acid, forming a solution from which the white oxychloride is precipitated by water.

In trying the effect of reagents on solutions of oxide of antimony, it is convenient to employ tartar emetic, from its property of dissolving in pure water without decomposition. From a solution of this salt, when moderately concentrated, a little pure potassa throws down the oxide as a white hydrate, but excess of the alkali redissolves the precipitate. The oxide is more perfectly separated by alkaline carbonates. Lime water causes a white precipitate, a mixed tartrate of lime and oxide of antimony; and earthy and metallic salts decompose tartar emetic by forming, like lime, sparingly soluble compounds with tartaric acid. Decomposition is also occasioned by most acids, which throw down a sparingly soluble salt of antimony and cream of tartar; and a recently made, pretty strong, infusion of gall-nuts gives a yellowish-white precipitate, which consists of tannic acid and oxide of antimony. But these appearances are by no means to be relied on as tests of the presence of antimony: a mixture of other substances might be similarly influenced by the same reagents; in a moderately dilute solution of tartar emetic most of them produce no effect whatever; and the too free addition of a pure alkali or of an acid, even to a strong solution, may altogether prevent that precipitate from forming, which a smaller quantity of the same reagents would have produced. The only certain method of bringing the antimony into view, even in a very weak solution, is to acidulate with tartaric acid, and then transmit through the liquid a current of hydrosulphuric acid gas. The hydrated tersulphuret of antimony, of a characteristic orange-red colour, is immediately formed.

The detection of antimony in mixed fluids, as when tartar emetic is mixed with articles of food, is conducted in the following manner:—The substances are first digested in water acidulated with about a drachm of hydrochloric and tartaric acids, which coagulate some organic matters, and give complete solubility to the oxide of antimony. Through the filtered liquid hydrosulphuric acid is then transmitted, when the orange-red tersulphuret of antimony subsides, which preserves its characteristic tint even when deposited from coloured solutions, and may be further recognized by solution in hot hydrochloric acid and precipitation by water. The metal itself may in general be obtained by placing the dry sulphuret in a glass tube, transmitting through it a current of hydrogen gas, and then, when all the atmospheric air is displaced, heating the sulphuret by the flame of a spirit-lamp. The sulphur is carried off in the form of hydrosulphuric acid gas, and the metallic antimony, recognizable by its lustre, remains. The metal is principally found where the sulphuret lay; but if the current of gas during the reduction happen to be rapid, it causes mechanically a spurious sublimation of antimony, which lines part of the tube with a thin film of metal. When much organic matter is mixed with the sulphuret, the metal is sometimes indistinctly seen. In that case it should be dissolved in a few drops of nitro-hydrochloric acid with heat, and be precipitated by water: it may then be redissolved by tartaric acid, and again precipitated with its characteristic tint by hydrosulphuric acid. Orfila recommends that the metal should be obtained from the sulphuret by fusion with black flux; but I have elsewhere shewn this process to be very precarious, and my opinion is supported by the experience of Christison. (Treatise on Poisons, 2nd ed., 429.) It may be detected, when present even in small quantity, by decomposing the antimoniuretted hydrogen formed as described under Arsenic, where the characters by which it is distinguished from arsenic are given.

Its eq. is 153·2; symb. $Sb + 3O$, $\dddot{Sb}$, or SbO_3.

Antimonious Acid.—When metallic antimony is digested in strong nitric acid, the metal is oxidized at the expense of the acid, and hydrated antimonic acid is formed; and on exposing this substance to a red heat, it gives out water and oxygen gas, and is converted into antimonious acid. It is also generated when the oxide is exposed to heat in open vessels. Thus, on heating sulphuret of antimony with free exposure to the air, sulphurous acid and oxide of antimony are generated; but on continuing the roasting after all the sulphur is burned, the oxide gradually absorbs oxygen and passes into antimonious acid. Hence this acid is formed in the process of preparing the *pulvis antimonialis* of the Pharmacopœia. Antimonious acid is white while cold, but acquires a yellow tint when heated, is very infusible, and fixed in the fire, two characters by which it is readily distinguished from the oxide. It is insoluble in water, and likewise in acids after being heated to redness. It combines in definite proportions with alkalies, and its salts are called *antimonites.* Antimonious acid is precipitated from these salts by acids as a hydrate, which reddens litmus paper, and is dissolved by hydrochloric and tartaric acids, though without appearing to form with them definite compounds.

Its eq. is 161·2; symb. $Sb + 4O$, $\ddddot{Sb}$, or SbO_4.

Antimonic Acid, sometimes called *peroxide* of antimony, is obtained as a white hydrate, either by digesting the metal in strong nitric acid, or by dissolving it in nitro-hydrochloric acid, concentrating by heat to expel excess of acid, and throwing the solution into water. When recently precipitated it reddens litmus paper, and may then be dissolved in water by means of hydrochloric or tartaric acid. It does not enter into definite combination with acids, but with alkalies forms salts, which are called *antimoniates*. When the hydrated peroxide is exposed to a temperature of 500° or 600° F. the water is evolved, and the anhydrous acid of a yellow colour remains. In this state it resists the action of acids. When exposed to a red heat, it parts with oxygen, and is converted into antimonious acid.

Its eq. is 169·4; symb. $Sb + 5O$, $\overset{.\,\dot{}\,.\,\dot{}\,.}{\mathrm{Sb}}$, or SbO_5.

Chlorides of Antimony.—When antimony in powder is thrown into a jar of chlorine gas, combustion ensues, and terchloride of antimony is generated. The same compound may be formed by distilling a mixture of antimony with about twice and a half its weight of corrosive sublimate, when the volatile terchloride of antimony passes over into the recipient, and metallic mercury remains in the retort. At common temperatures it is a soft solid, thence called *butter of antimony*, which is liquefied by gentle heat, and crystallizes on cooling. It deliquesces on exposure to the air; and when mixed with water, hydrochloric acid and sesquioxide are generated, and the latter, combined with undecomposed chloride, subsides.

Its eq. is 235·46; symb. $Sb + 3Cl$, or $SbCl_3$.

The *quadrichloride of antimony* is formed by acting on hydrated antimonious acid by hydrochloric acid; when a solution is formed, which appears to be a compound of bichloride of antimony and hydrochloric acid. It possesses little permanence, and on the addition of water antimonious acid subsides, and hydrochloric acid remains in solution.

The *perchloride* is generated by passing dry chlorine gas over heated metallic antimony. It is a transparent volatile liquid, which emits fumes on exposure to the air. Mixed with water, it is converted into hydrochloric acid and hydrated antimonic acid, which subsides. (Rose, in the Annals of Philosophy, N. S., x.)

Bromide of Antimony.—The union of bromine and antimony is attended with disengagement of heat and light, and the compound is readily obtained by distillation, as in the process for preparing bromide of arsenic. It is solid at common temperatures, is fused at 206°, and boils at 518° F. It is colourless, and crystallizes in needles; it attracts moisture from the air, and is decomposed by water.

Tersulphuret of Antimony.—Syn. Sesquisulphuret.—This is by far the most abundant ore of antimony, and is hence employed in making the preparations of this metal. Though often compact or earthy, it sometimes occurs in acicular crystals and in rhombic prisms. Its sp. gr. is 4·62, colour iron-grey, and its lustre metallic. When heated in close vessels, it enters into fusion without undergoing any other change. It may be formed artificially by fusing together antimony and sulphur, or by transmitting a current of hydrosulphuric acid gas through a solution of tartar emetic: in this case it falls as a hydrate of an orange-red colour, and does not acquire its dark colour till its water is expelled by heat. A large vein of this valuable mineral has been recently, 1846, discovered on the property of the Marquis of Bute, in Ayrshire. Gregory found the specimens examined by him from this vein to be free from arsenic.

Its eq. is 177·5; symb. $Sb + 3S$, or SbS_3.

The *bisulphuret* is formed, according to Rose, by transmitting hydrosulphuric acid gas through a solution of antimonious acid in dilute hydrochloric acid. (An. of Phil., N. S., x.)

Its eq. is 193·6; symb. $Sb + 4S$, or SbS_4.

Rose formed the *persulphuret* by the action of hydrosulphuric acid on a solution of antimonic acid. The golden sulphuret, prepared by boiling sulphuret of antimony and sulphur in solution of potassa, a process which is not adopted by either of our colleges, is a persulphuret.

Its eq. is 209·7; symb. $Sb + 5S$, or SbS_5.

Oxychloride of Antimony.—This compound has lately been studied by Malaguti and Johnston. When an acid solution of the terchloride of antimony is thrown into a large quantity of water, a white voluminous precipitate forms. Allowing it to subside, it contracts considerably during thirty or forty hours, and then consists of a thick bed of minute crystals. These crystals are small prismatic needles, of a white colour and brilliant lustre; they are decomposed by boiling in water, by continued washings, and by the alkaline carbonates, being thus converted into teroxide. They have been analyzed by Johnston, according to whom they are composed of 2 eq. of the terchloride united with 9 eq. of the teroxide; a composition which corresponds closely with the analysis of Malaguti.

Hence the eq. is 1949·72; symb. $2SbCl_3 + 9SbO_3$.

Oxysulphuret of Antimony.—Hist. and Prep.—Rose has shewn that this compound occurs in the mineral kingdom, being the *red antimony ore* (rothspiessglanzerz) of mineralogists. The pharmaceutic preparations known by the terms *glass*, *liver*, and *crocus* of antimony, are of a similar nature, though less definite in composition. They are made by roasting the native sulphuret, so as to form sulphurous acid and oxide of antimony, and then vitrifying the oxide together with undecomposed ore, by means of a strong heat. The product will of course differ according as more or less of the sulphuret escapes oxidation during the process.

When sulphuret of antimony is boiled in a solution of potassa or soda, a liquid is obtained, from which on cooling an orange-red matter called *Kermes mineral* is deposited ; and on subsequently neutralizing the cold solution with an acid, an additional quantity of a similar substance, the *golden sulphuret* of the Pharmacopœia, subsides. These compounds may also be obtained by igniting sulphuret of antimony with an alkali or alkaline carbonate, and treating the product with hot water ; or by boiling the mineral in a solution of carbonate of soda or potassa. The finest kermes is obtained, according to M. Cluzel, from a mixture of four parts of sulphuret of antimony, 90 of crystallized carbonate of soda, and 1000 of water. These materials are boiled for half or three-quarters of an hour ; the hot solution is filtered into a warm vessel, in order that it may cool slowly ; and after 24 hours the deposit is collected on a filter, moderately washed with cold water, and dried at a temperature of 70° or 80° F.

Prop.—Very great diversity of opinion has long existed among chemists as to the nature of kermes. Berzelius and Rose gave experiments to show that it is a hydrated tersulphuret, differing from the native sulphuret solely in being combined with water. Subsequently Gay-Lussac and others observed that kermes contains oxide of antimony, which may be removed by digestion with cream of tartar ; and Gay-Lussac inferred from the quantity of water formed when kermes, previously rendered anhydrous, is reduced by hydrogen gas, that it is a hydrated oxysulphuret, identical, when deprived of its water, with the red ore of antimony above referred to. Still more recently Berzelius has explained that the ordinary process for making kermes leads to the separation of a compound of oxide of antimony and potassa, which tenaciously adheres to kermes, but is not chemically united with it: he rightly argues that the question is not, whether oxide of antimony is sometimes or generally present in kermes, but whether the latter can exist *without* oxide of antimony. This question he has answered affirmatively. He fused sulphuret of antimony with black flux, boiled the residue in water, and set aside the solution to cool : a perfect kermes was deposited, which he considers, and I apprehend with good reason, to be quite free from oxide of antimony. (Pog. Annalen, xx. 364.)

The theory of the preparation of kermes, as given by Berzelius, is the following:—When tersulphuret of antimony is fused with potassa, part of each interchanges elements with the other in such a ratio that

1 eq. Tersulphuret of Ant.	SbS_3	yield	1 eq. Teroxide of Antimony	SbO_3
and 3 eq. Potassa	$3KO$		and 3 eq. Sulphuret of Potassium	$3KS$.

The sulphuret of potassium unites with undecomposed tersulphuret of antimony, forming a sulphur-salt, which will be again referred to hereafter, and teroxide of antimony with undecomposed potassa; and on adding hot water both compounds are dissolved, and coexist independently of each other in the solution. As the solution cools, the tersulphuret of antimony subsides, simply because the solvent power of sulphuret of potassium is thereby diminished; but a variable quantity of potassa and teroxide of antimony falls with the deposit, and cannot be entirely removed by washing with water. The cold solution still contains a double sulphuret of antimony and potassium, together with teroxide of antimony united with potassa: on acidulating with sulphuric acid, the sulphuret of potassium is resolved, by decomposition of water, into potassa and hydrosulphuric acid, and the teroxide of antimony is deprived of its potassa; and therefore the tersulphuret and teroxide of antimony, both losing at the same instant the principles which gave them solubility, are thrown down either in combination or in mixture with each other. Berzelius believes the same change to occur when the ingredients are boiled instead of fused together. The golden sulphuret differs from kermes, in the absence of potassa, in containing more oxide of antimony, and perhaps in being or containing an oxysulphuret. It commonly contains free sulphur, derived apparently from the oxidizing influence of the air on the sulphuret of potassium. When alkaline carbonates are employed instead of pure alkalies, the same phenomena ensue, except that carbonic acid is evolved.

Its eq. is 508·2; symb. $2Sb_2S_3 + Sb_2O_3$.

SECTION XIX.

URANIUM.—CERIUM.—LANTANIUM.

URANIUM.

Hist. and Prep.—THIS metal was discovered in 1789 by the German analyst Klaproth, who named it after the new planet Uranus, the discovery of which took place in the same year. It was obtained from a mineral of Saxony, called from its black colour *pitchblende*, which consists of oxide of uranium more or less contaminated with sulphur, selenium, phosphoric acid, lime, magnesia, alumina, silica, vanadium, manganese, arsenic, bismuth, antimony, zinc, tin, lead, iron, cobalt, nickel, copper, and silver. The amount of oxide of uranium in the mineral varies from 40 to 95 per cent. From this ore the uranium may be conveniently extracted by the following process:—After heating the mineral to redness, and reducing it to fine powder, it is digested in pure nitric acid diluted with three or four parts of water, taking the precaution to employ a larger quantity of the mineral than the nitric acid present can dissolve. By this mode of operating, the oxide, which has the formula U_3O_4, is converted into peroxide of uranium, U_2O_3, which unites with the nitric acid almost to the total exclusion of the iron. A current of hydrosulphuric acid gas is then transmitted through the solution, in order to separate arsenic and the other metals which are precipitated by that reagent. The solution is boiled to expel free hydrosulphuric acid, and after being concentrated by evaporation, is set aside to crystallize. The nitrate of peroxide of uranium is gradually deposited in flattened four-sided prisms of a beautiful lemon-yellow colour.

These may be further purified by dissolving them in ether, and allowing the etherial solution to evaporate in the air, when it deposits crystals of the pure salt, which are separated from the mother liquor, and again dissolved in water and crystallized. (Peligot.) The above is one of the easiest methods of extracting pure oxide of uranium from the ore; but a number of different processes have been given by Wittstein, Arfwedson, Ebelman, Lecanu and Serbat, Laugier, Werner, and others. For these I must refer to the Journals, or to Gmelin's Handbuch der Chemie, 4th edition, ii. 995.

The crystals of the nitrate when ignited leave the $\frac{3}{4}$ oxide, of a dark green colour. The metal was obtained, according to Arfwedson, by passing a current of hydrogen gas over this oxide at a red heat. But the recent researches of Peligot and of Ebelmen have shewn that in this way the metal cannot be obtained, and that the uranium of Arfwedson is really the protoxide, UO.

Metallic uranium is prepared according to Peligot in the following manner:—A mixture of about 50 grains of potassium and 100 of protochloride of uranium is heated in a small platinum crucible, the cover being tied down. The action is very violent, and in order to avoid danger from fragments of burning potassium, which are scattered about notwithstanding the precaution above recommended, the crucible should be placed within a larger one, also covered. After the incandescence is over, the crucible is to be strongly heated to expel any potassium that may be left uncombined; and when quite cold the mass is to be placed in cold water, as in the process for aluminium.

Wöhler dissolves in hydrochloric acid the compound of peroxide of uranium with ammonia, adds sal-ammoniac in excess, and an equal weight of sea-salt, dries up the mixture, and ignites it in a covered crucible till the sal-ammoniac is dissipated and the sea-salt melted, which protects the reduced metal from the action of the air. Water dissolves from the cooled mass the soluble chlorides, and leaves the metal undissolved.

Prop.—Metallic uranium appears partly as a black powder, partly fused at the sides of the crucible to silvery laminæ and fibrous threads, which may be filed, and seem to possess some ductility. (Peligot.) By Wöhler's method it is obtained as a black crystalline powder.

Its eq. is about 60; symb. U.

The compounds of uranium here described are the following:—

	Uranium.			Equiv.	Formulæ.
Protoxide .	60	1 eq.+Oxygen	8	1 eq.= 68	$U+O$ or UO.
$\frac{3}{4}$ Oxide .	180	3 eq.+ do.	32	4 eq.=212	$3U+4O$ or U_3O_4.
Peroxide .	120	2 eq.+ do.	24	3 eq.=144	$2U+3O$ or U_2O_3.
Protochloride .	60	1 eq.+Chlorine	35·42	1 eq.= 95·42	$U+Cl$ or UCl.
Protosulphuret	60	1 eq.+Sulphur	16	1 eq.= 46	$U+S$ or US.

Protoxide.—This is the substance formerly described as metallic uranium. It is obtained by passing hydrogen over the $\frac{3}{4}$ oxide at a red heat, or still better by treating in the same way the oxalate of the peroxide. According to Peligot there is first formed an oxide of the formula U_4O_5, and subsequently the protoxide, UO. It appears as a brown powder, or in the form of small copper-coloured octohedrons, possessing the metallic lustre. It is soluble in oil of vitriol with the aid of heat, yielding a green solution from which alkalies precipitate a bulky gelatinous hydrate of a brown colour, which if well washed with hot water retains its colour in the air. If, however, it retains ammonia from imperfect washing, it then attracts oxygen, and becomes yellow, yielding a compound of ammonia with the peroxide.

Its eq. is 68; symb. $U + O$, or UO.

Peligot is inclined to consider this oxide as a compound radical, playing the part of a metal. Thus he views the peroxide as a compound of 2 eq. of protoxide, $= U_2O_2$, and 1 eq. of oxygen; the 2 eq. of protoxide forming 1 eq. of the supposed radical uranyle, $= U_2O_2$, which he represents by Ul; and the peroxide by UlO. The chief arguments in favour of this view are the apparent tendency of the protoxide to unite with elementary bodies, such as chlorine, in the above proportion, and of the peroxide to form neutral salts with 1 eq. of acid. Thus, there exists an oxychloride, U_2O_2Cl, which Peligot considers as the protochloride of uranyle, UlCl. But there does not appear to be sufficient reason to adopt these views, which would introduce great complexity into the compounds of uranium, without any corresponding advantage.

$\frac{3}{4}$ *Oxide.—Syn. Green Oxide.*—This oxide, formerly considered the protoxide, is the chief ingredient of the pitchblende ore above mentioned. It is formed when the nitrate or carbonate of the peroxide is gently ignited, or when the protoxide is burned in the air. It is a powder of a dark olive-green colour, soluble in hot sulphuric acid, with which it forms a green solution. Its salts yield with alkalies a greyish-green hydrate, and are readily converted into persalts by the action of nitric acid, or even by exposure to the air.

Its eq. is 212; symb. $3U + 4O$, or U_3O_4.

According to Peligot's views, this oxide would be considered a compound of 3 eq. uranyle, and 2 eq. oxygen; $Ul_3O_2 = U_6O_6 + O_2 = U_6O_8 = 2\ (U_3O_4)$. But this is a most improbable formula; and the green oxide is most probably a compound of protoxide and peroxide; $UO + U_2O_3 = U_3O_4$.

When the green oxide, or indeed any oxide of uranium, is very strongly heated in the air, there is left a black oxide, containing rather less oxygen than the green oxide. Its composition is U_4O_5, and Peligot views it as a suboxide of uranyle, Ul_2O; but other chemists are disposed to regard it as a compound, or perhaps only a mixture of peroxide and protoxide, $U_2O_3 + 2UO = U_4O_5$; or protoxide and green oxide, $UO + U_3O_4 = U_4O_5$. It is most probably this oxide which gives the fine black colour to porcelain, for which oxide of uranium is now so much used. The green oxide is employed, but in the heat of the porcelain furnace it is most probably converted into the black oxide.

Peroxide.—Syn. Sesquioxide.—Uranic Acid.—This, the highest degree of oxidation of the metal, is obtained in several ways. By heating the double carbonate of ammonia and peroxide of uranium for a long time to 570°, the peroxide is left as a brick-red anhydrous powder. By evaporating at a temperature short of ebullition the solution of nitrate of uranium in absolute alcohol, till effervescence takes place, nitrous ether being given off, and washing the orange-yellow spongy residue with water to remove undecomposed nitrate, there is obtained the hydrate of the peroxide as a light powder of a very fine orange-yellow colour, which it communicates to most of its salts. It not only combines with acids, but likewise unites with alkaline bases, a property which was first noticed by Arfwedson. It is precipitated from acids as a yellow hydrate by pure alkalies, fixed or volatile; but retains a portion of these bases in combination. It is thrown down as a carbonate by alkaline carbonates, but is redissolved by an excess of carbonate of soda or ammonia, a circumstance which affords an easy method of separating uranium from iron. It is not precipitated by hydrosulphuric acid, but acquires a green tint from partial deoxidation. With ferrocyanuret of potassium it gives a brownish-red precipitate, very like ferrocyanuret of copper.

Peroxide of uranium is decomposed by a strong heat, and converted into the black oxide. From its affinity for alkalies, it is difficult to obtain it in a state of perfect purity. It is employed in the arts for giving an orange colour to porcelain.

Its eq. is 458 ; symb. $2U + 3O$, $\dddot{\underline{U}}$, or U_2O_3.

It is very remarkable that the formula of this oxide is the same on the new view of the compounds of uranium as on the old. When the present protoxide was viewed as the metal, and the green oxide as the protoxide, the atomic weight of the metal (now protoxide) was 217, which was, however, a little too high. But taking it at 204, it must be remembered that that number corresponds to 3 eq. of the present protoxide, $= U_3O_3$. If, therefore, we compare the three oxides, assuming in each U_3O_3, we perceive the following relations :—

Former Metal, now Protoxide.	Former Protoxide, now $\frac{3}{4}$ Oxide.	Peroxide.
U_3O_3.	$U_3O_3 + O$.	$U_3O_3 + O1\frac{1}{2}$.

On the present view these oxides are respectively

UO.	U_3O_4.	U_2O_3 or $UO1\frac{1}{2}$.

Thus it is evident that the relation between the oxygen in the former protoxide and that of the peroxide on the old view, is the same as that between the oxygen of the protoxide and that of the peroxide on the new view, namely, the relation of 1 to $1\frac{1}{2}$, or 2 to 3. The old formula, U_2O_3, for the peroxide, now represents $2(U_3O_3) + O_3$, or 3UlO, according to Peligot ; and its equivalent, of course, was 432. Now, U_2O_3 represents a body whose equivalent is 144 ; but the composition in 100 parts according to either formula is the same.

Protochloride—This compound, discovered by Peligot, is obtained by passing chlorine over a red-hot mixture of carbon with any oxide of uranium. It is deposited just beyond the hot part of the tube, in the form of dark green octohedrons, with metallic lustre, which at a red heat form a red vapour. It is soluble in water, apparently forming a hydrochlorate of the oxide.

Its eq. is 95·42 ; symb. $U + Cl$, or UCl.

When the protochloride is heated in a current of hydrogen, it loses one-fourth of its chlorine, and yields a subchloride, $4UCl + H = HCl + U_4Cl_3$. The subchloride is a dark brown fibrous mass, not volatile, very soluble in water; but the solution soon passes, with disengagement of hydrogen, into protochloride.

When chlorine is passed over red-hot protoxide of uranium, there is formed an oxychloride in yellow fusible crystals, which are very deliquescent. Their composition is $U_2O_2Cl = 2UO + Cl$. Peligot considers this body as chloride of uranyle, UlCl; but it is more probably either a compound of 2 eq. protoxide with 1 eq. chlorine, or peroxide in which 1 eq. oxygen is replaced by chlorine, $U_2 \left\{ \begin{matrix} O_2 \\ Cl \end{matrix} \right.$. Or it may be, as Berzelius thinks, a compound of peroxide and perchloride, $2U_2O_3 + U_2Cl_3 = 3\,(U_2O_2Cl)$. It would seem to be analogous to the oxychloride of chromium and others, formerly described.

Protosulphuret.—Metallic uranium, when heated with sulphur, combines with it; and the same compound is formed by passing bisulphuret of carbon over oxide of uranium at a red heat. It is black, with a tinge of yellow, and when rubbed exhibits metallic lustre. It is converted into protoxide when heated in the air, and is readily dissolved by nitric, but not by hydrochloric acid.

Its eq. is 76·12; symb. $U + S$, or US.

There appear to be more sulphurets of uranium. Alkaline sulphurets throw down from solutions of the green oxide a black precipitate, probably a sulphuret corresponding to that oxide, U_3S_4; and the same reagents produce in the salts of the peroxide a dark brown precipitate, probably a sesquisulphuret, U_2S_3.

CERIUM.—LANTANIUM.—DIDYMIUM.

Cerium, named after the planet Ceres, was discovered in the year 1803 by Hisinger and Berzelius, in a rare Swedish mineral known by the name of cerite, and its existence was recognized about the same time by Klaproth. Thomson has since found it to the extent of 34 per cent. in a mineral from Greenland called *allanite*, in honour of the late Mr. Allan, who first distinguished it as a distinct species.

Very lately, Mosander has shewn that the oxide commonly considered as oxide of cerium contains a large proportion of the oxide of a new metal, to which he has given the name of lantanium (from *λανθανω*, *I lurk*, it having lain concealed in the ores of cerium). The properties and compounds of this new metal have not yet been fully investigated, and of course those of pure cerium are equally unknown. There is, however, a great analogy between them, each forming two oxides, both of which unite with acids. The carbonates of both protoxides are white and insoluble; the sulphates soluble and crystallizable.

By the following process the two oxides may be conveniently separated:—The mixed oxide is dissolved in nitric acid, the solution evaporated to dryness, and the residue calcined. The oxide is now powdered, and digested in weak nitric acid (1 of acid to 50 or 100 of water), which dissolves the oxide of lantanium, and leaves the oxide of cerium undissolved. The former may be precipitated as carbonate by a carbonated alkali; the latter may be dissolved by a strong acid, and also converted into carbonate. It would be absurd, in the present state of our knowledge, to give details as to the compounds of these two metals, which cannot possibly be correct. Indeed, the last researches of Mosander have demonstrated the existence in the ores of cerium as well as in those of yttrium of another new metal, to which he has given the name of didymium. He has not yet succeeded in obtaining any one of these metals perfectly pure; and as they seem to be frequently accompanied with the new metals erbium and terbium, the difficulty becomes very great indeed. We must therefore be content to announce the existence of cerium, lantanium, and didymium, and to wait for a fuller and more accurate account of them till the researches of Mosander are completed. It would appear that the amethyst colour frequently observed in the salts of yttrium, and sometimes in those of cerium, depends on the presence of some of these imperfectly studied metals.

The symbol of cerium is Ce; that of lantanium will be La, and that of Didymium D. Both metals are more closely allied to yttrium and zirconium than to any others.

SECTION XX.

BISMUTH.—TITANIUM.—TELLURIUM.

BISMUTH.

Hist. and Prep.—This metal was known to the ancients, though often confounded by them with lead and tin; but it appears to have obtained the name of *bismuth*, or properly *wismuth*, from the German miners. It occurs in the earth both native and in combination with other substances, such as sulphur, oxygen, and arsenic. That which is employed in the arts is derived chiefly from native bismuth, and commonly contains small quantities of sulphur, iron, and copper.

It may be obtained pure for chemical purposes by heating the oxide or subnitrate to redness along with charcoal.

Prep.—Bismuth has a reddish-white colour and considerable lustre. Its structure is highly lamellated, and when slowly cooled it crystallizes in cubes or octohedrons. Its density is about 10. It is brittle when cold, but may be hammered into plates while warm. At 476° it fuses, and sublimes in close vessels at a red heat. It is a less perfect conductor of heat than most other metals.

Bismuth undergoes little change by exposure to air at common temperatures. When fused in open vessels, its surface becomes covered with a grey film, which is a mixture of metallic bismuth with the oxide of the metal. Heated to its subliming point, it burns with a bluish-white flame, and emits copious fumes of oxide of bismuth. The metal is attacked with difficulty by hydrochloric or sulphuric acid, but it is readily oxidized and dissolved by nitric acid.

The eq. of bismuth, deduced from the composition of its oxide, is 213; its symb. is Bi. Its compounds described in this section are thus constituted:—

	Bismuth.			Equiv.	Formulæ.
Oxide .	213	1 eq.+Oxygen	24	3 eq.=237	$Bi+3O$ or BiO_3.
Peroxide	213	2 eq.+ do.	40	5 eq.=253	$Bi+5O$ or BiO_5.
Chloride	213	1 eq.+Chlorine	106·26	3 eq.=319·26	$Bi+3Cl$ or $BiCl_3$.
Bromide	213	1 eq.+Bromine	225·2	3 eq.=438·2	$Bi+3Br$ or $BiBr_3$.
Sulphuret	213	1 eq.+Sulphur	48·3	3 eq.=261·3	$Bi+3S$ or BiS_3.

Oxide of Bismuth.—This compound is readily prepared by heating to redness the nitrate or subnitrate of oxide of bismuth. Its colour is yellow; at a full red heat it is fused into a brown liquid, which on cooling becomes a crystalline mass, but if the fusion be made in an earthen crucible, silica is taken up, and it then forms a yellow transparent glass of sp. gr. 8·211. At intense temperatures it is sublimed. It unites with acids, and most of its salts are white.

When nitrate of oxide of bismuth, either in solution or in crystals, is put into water, a copious precipitate, the subnitrate, of a beautifully white colour, subsides, which was formerly called the *magistery of bismuth.* From its whiteness it is sometimes employed as a paint for improving the complexion; but it is an inconvenient cosmetic, owing to the facility with which it is blackened by hydrosulphuric acid. If the nitrate with which it is made contains no excess of acid, and a large quantity of water is employed, nearly the whole of the bismuth is separated as a subnitrate. By this character bismuth may be both distinguished and separated from other metals.

Its eq. is 237; symb. $Bi + 3O$, $\overset{\cdots}{Bi}$, or BiO_3.

Peroxide.—Syn. Bismuthic Acid.—This oxide was first noticed by Bucholz and Brandes, but its nature and composition have been recently examined by Stromeyer, Jacquelin, and Frémy. It is generated when hydrate of soda is fused at a moderate heat with oxide of bismuth, and is purified by boiling with solution of soda, and washing the brown insoluble powder first with nitric acid, and then with water.

As thus prepared, peroxide of bismuth is a heavy powder of a brown colour, very like peroxide of lead, manifests little disposition to unite either with acids or alkalies, and is reconverted by heat with loss of oxygen into the oxide. Heated with sulphuric or phosphoric acid, it gives off oxygen gas, and a sulphate or phosphate of the oxide is formed; and with hydrochloric acid chlorine is evolved, and the chloride produced. (An. de Ch. et Ph. li. 267.)

Its eq. is 253; symb. $Bi + 5O$, $\overset{\cdot\cdot\cdot\cdot\cdot}{Bi}$, or BiO_5.

Chloride of Bismuth.—When bismuth in fine powder is introduced into chlorine gas, it takes fire, burns with a pale blue light, and is converted into a chloride, formerly termed *butter* of bismuth. It may be prepared conveniently by heating two parts of corrosive sublimate with one of bismuth, and afterwards expelling the excess of the former, together with the metallic mercury, by heat.

Chloride of bismuth is of a greyish-white colour, opaque, and of a granular texture. It fuses at a temperature a little above that at which the metal itself is liquefied, and bears a red heat in close vessels without subliming.

Its eq. is 319·26; symb. $Bi + 3Cl$, or $BiCl_3$.

Bromide of Bismuth is prepared by heating the metal with a large excess of bromine in a long tube; when a grey-coloured bromide results, similar in its aspect to fused iodine. At 392° it enters into fusion, and at a low red heat sublimes. With water it is converted into oxide of bismuth and hydrobromic acid, the former of which combines with some undecomposed bromide of bismuth as an oxybromide. (Serullas.)

Sulphuret of Bismuth.—This sulphuret is found native, and may be formed artificially by fusing bismuth with sulphur, or by the action of hydrosulphuric acid on the salts of bismuth. It is of a lead-grey colour and metallic lustre.

Its eq. is 261·3; symb. $Bi + 3S$, or BiS_3.

TITANIUM.

Hist.—This metal was first recognised as a new substance by Mr. Gregor of Cornwall, and its existence was afterwards established by Klaproth, who fancifully gave it the name of *Titanium*, after the

Titans of ancient fable. (Contributions, i.) But the properties of the metal were not ascertained in a satisfactory manner until the year 1822, when Wollaston was led to examine some minute crystals which were found in a slag at the bottom of a smelting furnace at the great iron-works at Merthyr Tydvil in Wales, and presented to him by Buckland. (Philosophical Transactions, 1823.) These crystals, which have since been found at other iron-works, are of a cubic form, and in colour and lustre resemble burnished copper. They are found in the blast-furnaces, and are probably derived principally from the hearth-stone, which contains them abundantly. They conduct electricity, and are attracted slightly by the magnet, a property which seems owing to the presence of a minute quantity of iron. Their sp. gr. is 5·3; and their hardness is so great, that they scratch a polished surface of rock crystal. They are exceedingly infusible; but when exposed to the united action of heat and air, their surface becomes covered with a purple-coloured film, which is an oxide. They resist the action of nitric and nitro-hydrochloric acids, but are completely oxidized by being strongly heated with nitre. They are then converted into a white substance, which possesses all the properties of titanic acid.

Prep.—Liebig prepares metallic titanium by putting fragments of recently made chloride of titanium and ammonia into a glass tube half an inch wide and two or three feet long, transmitting through it a current of perfectly dry ammonia, and when atmospheric air is entirely displaced, applying heat until the glass softens. Complete decomposition ensues, nitrogen gas is disengaged, hydrochlorate of ammonia sublimes, and metallic titanium is left in the state of a deep blue-coloured powder. If exposed to the air while warm, it is apt to take fire. It is possible that the powder thus prepared may be not pure titanium, but a compound of the metal with nitrogen.

The eq. of titanium, determined by Rose from his analysis of the bichloride, is 24·3; its symb. is Ti. The composition of its compounds described in this section is as follows:—

	Titanium.			Equiv.	Formulæ.
Sesquioxide	48·6	2 eq.+Oxygen	24	3 eq.=72·6	$2\,Ti+3O$ or Ti_2O_3.
Titanic Acid	24·3	1 eq.+ do.	16	2 eq.=40·3	$Ti+2O$ or TiO_2.
Bichloride .	24·3	1 eq.+Chlorine	70·84	2 eq.=95·14	$Ti+2Cl$ or $TiCl_2$.
Bisulphuret	24·3	1 eq.+Sulphur	32·24	2 eq.=56·54	$Ti+2S$ or TiS_2.

Sesquioxide of Titanium.—When titanic acid is exposed to a strong heat in a black-lead crucible, a mass is obtained, the exterior crust of which is metallic titanium, but the interior parts consist of the supposed protoxide. As thus prepared it is a black mass, which has an earthy fracture, is quite insoluble in all acids, and is very difficult to oxidize. Sesquioxide of titanium is formed in the moist way, when a fragment of zinc or iron is introduced into a solution of titanic acid in hydrochloric acid. The solution soon acquires a purple tint, and after a time the whole of the titanic acid is deoxidized and thrown down in the form of a deep purple powder. This cannot be collected, owing to the facility with which it is reconverted into titanic acid; hence its composition and chemical properties are little known; but Rose, by his elaborate and ingenious researches into the constitution of the mineral called titanate of iron, has rendered it nearly certain that that mineral is a compound of sesquioxide (peroxide) of iron with sesquioxide of titanium, and that the blue oxide of titanium is a true sesquioxide, analogous to the sesquioxides of tin, iron, chromium, &c., and isomorphous with sesquioxide of iron.

On this view, its eq. is 72·6; symb. $2Ti + 3O$, $\overset{\cdots}{\underline{Ti}}$, or Ti_2O_3.

Titanic Acid.—Hist. and Prep.—This compound, called also peroxide of titanium, has been carefully studied by H. Rose, who first pointed out its acid properties. It occurs in a nearly pure state in the minerals brookite, rutile, and anatase, which are remarkable for presenting the same chemical compound crystallized in three unconnected forms, and of different specific gravities. It also exists in titanite or sphene as titanate and silicate of lime, and in menaccanite as titanate of the oxides of iron and manganese, in the latter of which titanium was originally discovered by Gregor. It is best prepared from rutile, which is essentially titanic acid, sometimes quite pure, but more frequently contaminated with from 0·25 to 2 per cent. of oxides of iron and manganese. The mineral, after being reduced to an exceedingly fine powder, is fused in a platinum crucible with three times its weight of carbonate of potash, and the mass afterwards washed with water to remove the excess of alkali. A grey mass remains, which consists of potash and titanic acid. This compound is dissolved in concentrated hydrochloric acid; and on diluting with water, and boiling the solution, the greater part of the titanic acid is thrown down. It is then collected on a filter, and well washed with water acidulated with hydrochloric acid. In this state it is not quite pure; but contains a little oxide of manganese and iron, derived from the rutile. The best mode of separating these impurities is to digest the precipitate, while still moist, with hydrosulphate of ammonia, which converts the oxides of iron and manganese into sulphurets, but does not act on the titanic acid. The two sulphurets are readily dissolved by dilute hydrochloric acid; and the titanic acid, after being collected on a filter and well washed as before, may be dried and heated to redness. This method, proposed by Rose of Berlin, has been thus simplified by himself. Either rutile or titaniferous iron, after being pulverized and washed, is exposed in a porcelain tube at a very strong red heat to a current of hydrosulphuric acid gas, which acts upon the oxide of iron, giving rise to water and sulphuret of iron. As soon as water ceases to appear the process is discontinued, the mass digested in hydrochloric acid to remove the iron, and the titanic acid separated from adhering sulphur by heat. A little iron is still usually retained; but the whole may be removed by a repetition of the same process. (An. de Ch. et Ph. xxiii. and xxxviii. 131.)

Prop.—Titanic acid, when pure, is quite white, although it may acquire a brown colour without the presence of any impurity. Thus, when precipitated by ammonia from its solution in hydrochloric or sulphuric acids, pure titanic acid yields a bulky hydrate, which when dried and ignited is brown, exactly like the purest specimens of rutile. This peculiarity is connected with the differences of density and of crystalline form in the three mineral forms of the acid; for Rose has obtained, in artificial specimens, the same variety of specific gravity as in the native acid. Anatase, corresponding to the white acid, has a sp. gr. of about 3·8: the sp. gr. of brookite is about 4·1; and that of rutile is about 4·25: and Rose has shewn that the artificial acid, at first of sp. gr. 3·6, when exposed to a long-continued heat, became denser, and at last acquired the sp. gr. 4·25 and the colour of rutile. It is exceedingly infusible; and after being once ignited it ceases to be soluble in acids, except in the hydrofluoric. In its chemical relations it is analogous to silicic acid, being a feeble acid, insoluble in water, without action on test paper, but combining with metallic oxides. In the state of hydrate, as when precipitated from hydrochloric acid by boiling, or when combined with an alkali after fusion, it has a singular tendency to pass through the pores of a filter when washed with pure water; but the presence of a little acid, alkali, or salt prevents this inconvenience.

If previously ignited with carbonate of potassa, titanic acid is soluble in dilute hydrochloric acid; but it is retained in solution by so feeble an attraction, that it is precipitated merely by boiling. It is likewise thrown down by the pure and carbonated alkalies, both fixed and volatile. A solution of gall-nuts causes an orange-red colour, which is very characteristic of titanic acid; an effect which appears owing to tannic, and not to gallic acid. When a rod of zinc is suspended in the solution, a purple-coloured powder, probably the sesquioxide, is precipitated, which is gradually converted into titanic acid.

Its eq. is 40·3; symb. $Ti + 2O$, $\ddot{Ti}$, or TiO_2.

Bichloride of Titanium.—This substance was discovered in the year 1824 by Mr. George of Leeds, by transmitting dry chlorine gas over metallic titanium at a red heat. Rose prepared it for his analysis by heating a mixture of titanic acid and charcoal in a tube, through which dry chlorine gas was passing: the resulting bichloride was purified from adhering free chlorine by agitation either with mercury or potassium, and repeated distillation. At common temperatures it is a transparent colourless fluid, of considerable sp. gr., boils violently at a temperature a little above 212°, and condenses again without change. Dumas has shewn that the density of its vapour may be estimated at 6·615. In open vessels it is attacked by the moisture of the atmosphere, and emits dense white fumes of a pungent odour similar to that of chlorine, but not so offensive. On adding a few drops of water to a few drops of the liquid, combination ensues with almost explosive violence, from the evolution of intense heat; and if the water is not in excess, a solid hydrate is obtained. On exposure to the air it deliquesces, and on adding water the greater part is dissolved. The bichloride, when exposed to an atmosphere of dry ammonia, absorbs a large quantity of the gas, and is converted into a brown or yellow solid. It was from this compound Liebig prepared metallic titanium, as above described.

Its eq. is 95·14; symb. $Ti + 2Cl$, or $TiCl_2$.

Bisulphuret of Titanium.—This compound was discovered by Rose, who prepared it by transmitting the vapour of bisulphuret of carbon over titanic acid, heated to whiteness in a tube of porcelain. It occurs in thick green masses, which by the least friction acquire a dark yellow colour and metallic lustre. When heated in the open air it is converted into sulphurous and titanic acids. By acids it is slowly decomposed, and is dissolved by hydrochloric acid with disengagement of hydrosulphuric acid gas.

Its eq. is 56·5: symb. $Ti + 2S$, or TiS_2.

TELLURIUM.

Hist.—A rare metal, hitherto found only in the gold mines of Transylvania, and even there in very small quantity. Its existence was inferred by Müller in the year 1782, and fully established in 1798 by Klaproth, who gave it the name of *tellurium*, from *tellus*, the earth, suggested by the source from which he drew the name of uranium. (Contributions, iii.) It occurs in the metallic state, chiefly in combination with gold, silver, and bismuth.

Prop.—It has a tin-white colour running into lead-grey, a strong metallic lustre, and lamellated texture. It is very brittle, and its density is 6·2578. It fuses at a temperature below redness, and at a red heat is volatile. When heated before the blowpipe, it takes fire, burns rapidly with a blue flame bordered with green, and is dissipated in grey-coloured pungent inodorous fumes. The odour of decayed horse-radish is sometimes emitted during the combustion, and was thought by Klaproth to be peculiar to tellurium; but Berzelius ascribes it solely to the presence of selenium.

From some experiments of Berzelius the eq. of tellurium is 64·2; its symb. is Te. The compounds described in this section are thus constituted:—

	1 eq. Tellurium.		Equiv.	Formulæ.
Tellurous Acid .	64·2+Oxygen	16	2 eq.= 80·2	$Te+2O$ or TeO_2.
Telluric Acid .	64·2+ . .	24	3 eq.= 88·2	$Te+3O$ or TeO_3.
Chloride . .	64·2+Chlorine	35·42	1 eq.= 99·62	$Te+Cl$ or $TeCl$.
Bichloride .	62·2+ . .	70·84	2 eq.=135·04	$Te+2Cl$ or $TeCl_2$.
Bisulphuret .	64·2+Sulphur	32·2	2 eq.= 96·4	$Te+2S$ or TeS_2.
Persulphuret .	Composition uncertain.			
Hydrotelluric Acid	64·2+Hydrogen	1	1 eq.= 65·2	$H+Te$ or HTe.

Tellurous Acid.—This compound, also called *oxide of tellurium*, is generated by the action of nitric acid on tellurium, by which acid it is dissolved; but the solution possesses so little permanence that mere effusion of water precipitates part of it, and the rest is obtained by evaporating to dryness. In this state it is a white granular anhydrous powder, which slowly reddens moist litmus paper, and is insoluble in water and acids. By pure potassa or soda in solution it is dissolved, and is rendered soluble by fusion with the alkaline carbonates, forming with those alkalies crystallizable salts. Acids added in slight excess to the alkaline solutions throw down tellurous acid as a white flaky hydrate, which if washed in ice-cold water, and dried at a temperature not exceeding 53°, may be preserved unchanged. In this state it is freely soluble in acids, in ammonia, in the alkaline carbonates, from which it expels carbonic acid, and even to considerable extent in pure water. Its aqueous solution reddens litmus paper: it becomes turbid at 68°, and the acid which falls is no longer soluble in acids. In these properties tellurous acid closely resembles the titanic and several other feeble acids, which have a soluble hydrated state easily convertible into an insoluble anhydrous one. Its salts are precipitated black by hydrosulphuric acid, bisulphuret of tellurium being formed. It is deoxidized, and metallic tellurium falls as a black powder, when a piece of zinc, tin, iron, or antimony is left in its solution. Its eq. is 80·2; symb. $Te + 2O$, $\ddot{T}e$, or TeO_2.

Telluric Acid.—The process which Berzelius recommends for preparing this compound is either to deflagrate tellurous acid with nitre, or to mix pure potassa freely with a solution of tellurite of potassa, and to saturate fully with chlorine. Nitric acid in slight excess and a little chloride of barium are added, in order to precipitate any traces of sulphuric or selenic acids; and after separating the precipitate by filtration, the liquid is exactly neutralized with ammonia, and chloride of barium added as long as it causes a precipitate. The tellurate of baryta is washed, dried by a gentle heat, and then digested with a fourth of its weight of strong sulphuric acid previously diluted with water: the filtered solution is then concentrated by a water bath, and on cooling or subsequent spontaneous evaporation yields hydrated telluric acid in the form of flat six-sided prisms. Adhering sulphuric acid is removed by alcohol.

This hydrate consists of 1 eq. of acid and 3 eq. of water. When heated at 212° it loses 2 of its eq. of water; and on heating still further all its water is expelled, and the anhydrous acid of a lemon-yellow colour remains. In this state it is insoluble in all fluids, whereas the hydrated acid is soluble in water; and the salts of the former differ from those which the latter forms with the same bases. Hence heat modifies the character of telluric acid much in the same way as that of phosphoric acid. At a heat beyond that required to render it anhydrous, telluric acid loses oxygen and is reduced to tellurous acid. (Pog. Annalen, xxviii. 392.)

Its eq. is 88·2; symb. $Te + 3O$, $\dddot{Te}$, or TeO_3.

Chloride.—Rose obtained it by passing a feeble current of chlorine gas over tellurium at a strong heat, when the chloride passes over as a violet vapour, which at first condenses into a black liquid, and when quite cold becomes a solid of the same colour. By the action of water it deposits metallic tellurium, and the bichloride is dissolved.

Its eq. is 99·62; symb. $Te + Cl$, or $TeCl$.

Bichloride.—Rose obtained this in the same manner as the preceding chloride, except using a lower heat and a more liberal supply of chlorine. The bichloride is also volatile, and after being purified from free chlorine by agitation with mercury, and a second distillation, it condenses into a white crystalline solid. By a gentle heat it yields a brown liquid, but recovers its whiteness on cooling. (Pog. Annalen, xxi. 443.)

Its eq. is 135·04; symb. $Te + 2Cl$, or $TeCl_2$.

Bisulphuret.—This compound falls of a dark brown, nearly black colour, when hydrosulphuric acid gas is transmitted through a solution of bichloride of tellurium, tellurous acid, or any soluble tellurite.

This sulphuret is what Berzelius calls a sulphur-acid, forming a soluble sulphur-salt by uniting with sulphuret of potassium. Hence a solution of caustic potassa dissolves bisulphuret of tellurium, producing the same kind of change as on sulphuret of antimony.

Its eq. is 96·4; symb. $Te + 2S$, or TeS_2.

Persulphuret.—This compound falls of a deep yellow colour, when a salt of telluric acid is mixed in solution with persulphuret of potassium. Its existence is but transient, as it is quickly transformed into bisulphuret and becomes black.

Hydrotelluric Acid.—This gas, discovered by Davy in 1809, is formed by acting with hydrochloric acid on an alloy of tellurium with zinc or tin. It has the properties of a feeble acid, very analogous in odour, and apparently in composition, to hydrosulphuric and hydroselenic acids; it is absorbed by water, forming a claret-coloured solution; and it precipitates many metallic salts, yielding an alloy of tellurium with the other metal. It is deprived of its hydrogen by chlorine, nitric acid, or oxygen of the atmosphere, tellurium being separated.

Its eq. is 65·2; symb. $Te + H$, or TeH.

The existence of this compound, the property possessed by tellurium of forming a soluble compound with potassium, and the composition of the tellurous and telluric acids, indicate a very strong analogy between tellurium on the one hand, and sulphur and selenium on the other. These elements appear to form a group of three, as is also the case with phosphorus, arsenic, and antimony, and with chlorine, bromine, and iodine. This group forms a connexion between the metallic and non-metallic bodies; for, while sulphur is entirely destitute of the metallic character, and tellurium is evidently a metal, selenium is exactly intermediate; being classed as a metal by some chemists, and as a non-metallic body by others.

SECTION XXI.

COPPER.

Hist. and Prep.—One of the most abundant of the metals, and well known to the ancients. Native copper is by no means uncommon, being found more or less in most copper-mines: it occurs in large amorphous masses in some parts of America; and a hill of considerable size, entirely composed of metallic copper, is said to have been lately discovered in Australia. It is sometimes met with in octohedral crystals, or in some of the forms allied to the octohedron. Stromeyer has lately discovered it in several specimens of meteoric iron, but in a quantity not exceeding 2-1000ths of the mass. The copper of commerce is extracted chiefly from the native sulphuret; especially from copper pyrites, a double sulphuret of iron and copper. The first part of the process consists in roasting the ore, so as to burn off some of the sulphur, and leave the remainder as a subsulphate of the oxides of iron and copper. The mass is next heated with some unroasted ore and siliceous substances, by which means much of the iron unites in the state of black oxide with silicic acid, and rises as a fusible slag to the surface; while most of the copper returns to the state of sulphuret. It is then subjected to long-continued roasting, when the greater part of the sulphur escapes as sulphurous acid, and the metal is oxidized; after which it is reduced by charcoal, and more of the iron separated as a silicate by the addition of sand. Lastly, the metal is strongly heated while a current of air plays upon its surface: the impurities, chiefly sulphur and iron, being more oxidizable than copper, combine with oxygen by preference, and the copper is at length left in a state of purity sufficient for the purposes of commerce. A very pure copper is obtained from the native carbonate, a beautiful mineral, which occurs either in deep blue crystals, or in the more compact form of malachite, which is much prized as an ornamental stone for its fine green colour, and a large quantity of copper is procured from the water of many copper-mines, which, by the oxidation of sulphuret of copper, becomes gradually charged with sulphate of the protoxide or blue vitriol. The water, thus charged, is collected in tanks, into which is thrown a quantity of old iron. The iron is oxidized at the expense of the oxide of copper, and combines with the sulphuric acid, forming green vitriol, which may be obtained in crystals by evaporation, while the copper is deposited as a spongy metallic mass, which is very pure, and which it is only necessary to fuse, and run into moulds.

Prop.—Distinguished from all other metals, titanium excepted, by having a red colour. It receives a considerable lustre by polishing. Its density, when fused, is 8·667, and it is increased by hammering. It is both ductile and malleable, and in tenacity is inferior only to iron. It is hard and elastic, and consequently sonorous. Its point of fusion is 1996° F. according to Daniell, being less fusible than silver and more so than gold.

It undergoes little change in a perfectly dry atmosphere, but is rusted in a short time by exposure to air and moisture, being converted into a green substance, carbonate of the black oxide of copper. At a red heat it absorbs oxygen, and is converted into black scales of oxide. It is attacked with difficulty by hydrochloric and sulphuric acids, and not at all by solutions of the vegetable acids, if atmospheric air be excluded; but if air have free access, the metal absorbs oxygen with rapidity, the attraction of the acid for the oxide of copper co-operating with that of the copper for oxygen. It is important, on account of the poisonous quality of the solutions of copper, to bear in mind that the vegetable acids only dissolve copper in the cold. Consequently, although vegetable juices may be and are safely *boiled* in copper vessels, as in the making of jams and jellies, they must never, on any account, be allowed to cool in such vessels, or to remain in them after cooling, as, under these circumstances, they would infallibly dissolve sufficient copper to produce dangerous or even fatal effects. Nitric acid acts with violence on copper, forming a nitrate of the black oxide.

The most trustworthy experiments for determining the eq. of copper are those of Berzelius on the reduction of the black oxide by means of hydrogen gas at a red heat. According to the best of his analyses, 8 parts of oxygen unite with 31·6 parts of copper to constitute the black oxide; and, therefore, if this oxide be formed of an atom of oxygen united with an atom of copper, the eq. of this metal will be 31·6. This opinion, which I have adopted, is maintained by Thomson, Berzelius, and many Continental chemists. Others consider it as a binoxide, regarding red oxide of copper as the real protoxide; and these take twice 31·6 or 63·2 as an eq. of copper. The principal arguments in favour of the former view are these:—1, the red oxide has very much the character of a *suboxide*, a term frequently used to designate an oxide which has little or no tendency to unite with acids, and which contains less than one atom of oxygen to one atom of metal; 2, the product of the eq. and specific heat of most metals is a constant quantity, and copper coincides with the law, provided the black oxide contain an atom of each element; 3, the salts of the black oxide are ismorphous with the salts of protoxide of iron, which gives a strong presumption that these oxides possess the same atomic constitution.

Its symb. is Cu.

The composition of the compounds described in this section is as follows:—

	Copper.			Equiv.	Formulæ.
Red or Dinoxide	63·2	2 eq.+Oxygen	8	1 eq = 71·2	$2Cu+O$ or Cu_2O.
Black or Protoxide	31·6	1 eq.+ do.	8	1 eq.= 39·6	$Cu+O$ or CuO.
Superoxide . .	Composition uncertain.				
Nituret . .	189·6	6 eq.+Nitrogen	14	1 eq.=203·6	$6Cu+N$ or Cu_6N.
Dichloride . .	63·2	2 eq.+Chlorine	35·42	1 eq.= 98·62	$2Cu+Cl$.
Chloride . .	31·6	1 eq.+ do.	35·42	1 eq.= 66·02	$Cu+Cl$.
Diniodide . .	63·2	2 eq.+Iodine	126·3	1 eq.=189·5	$2Cu+I$.
Disulphuret . .	63·2	2 eq.+Sulphur	16·1	1 eq.= 79·3	$2Cu+S$.
Sulphuret .	31·6	1 eq.+ do.	16·1	1 eq.= 47·7	$Cu+S$.
Triphosphuret .	94·8	3 eq.+Phosphorus	15·7	1 eq.=110·5	$3Cu+P$.
Subsesquiphosph. .	94·8	3 eq.+ do.	31·4	2 eq.=126·2	$3Cu+2P$.

Red Oxide.—Hist. and Prep.—This compound occurs native in the form of octohedral crystals, and is found of peculiar beauty in the mines of Cornwall. It may be prepared artificially by heating in a covered crucible a mixture of 31·6 parts of copper filings with 39·6 of the black oxide; or still better, by arranging thin copper plates one above the other with interposed strata of the black oxide, and exposing them to a red heat carefully protected from the air. Another method is by boiling a solution of acetate of protoxide of copper with sugar, when the suboxide subsides as a red powder; and another is to fuse at a low red heat the dichloride of copper with about an equal weight of carbonate or bicarbonate of soda, subsequently dissolving the sea-salt by water, and drying the red powder.

In this case, by an interchange of elements,

1 eq. Dichloride of Copper	Cu_2Cl	yield	1 eq. Red Oxide	Cu_2O
and 1 eq. Soda	NaO		and 1 eq. Chloride of Sodium	$NaCl$.

Malaguti recommends the following process:—100 parts of sulphate of copper and 57 of carbonate of soda, both in crystals, are fused at a gentle heat; and the mass left when all water is expelled is pulverized and mixed with 25 parts of copper filings. The mixture is pressed into a crucible and exposed for 20 minutes to a white heat. The result is again pulverized and carefully washed. It has a fine red colour. (An. de Ch. et Ph. liv. 216.)

Prop.—The red oxide of copper has a sp. gr. of 6·093, and in colour is very similar to copper. It may be preserved in a dry atmosphere; but at a red heat it absorbs oxygen and is converted into the protoxide. Dilute acids act on it very slowly; and the resulting solution, as is indicated by its tint, does not arise from the union of the red oxide itself with the acid, but from its being resolved, like other sub-oxides, into metal and a protoxide. With strong nitric acid it is oxidized, binoxide of nitrogen escapes, and a nitrate of the black oxide is formed. Strong hydrochloric acid forms with it a colourless solution, from which alkalies throw it down as a hydrate of an orange tint. In this state it readily absorbs oxygen from the air. The red oxide of copper is soluble in ammonia, and the solution is quite colourless; but it becomes blue with surprising rapidity by free exposure to air, owing to the absorption of oxygen and formation of the black oxide.

Its eq. is 71·2; symb. $2Cu + O$, or Cu_2O.

Black Oxide.—Hist. and Prep.—This compound, the *copper black* of mineralogists, is sometimes found native, being formed by the spontaneous oxidation of other ores of copper. It may be prepared artificially by calcining metallic copper, by precipitation from the salts of copper by means of pure potassa, and by heating nitrate of copper to redness.

Prop.—It varies in colour from a dark brown to a bluish-black, according to the mode of formation: its sp. gr. is 6·401. It undergoes no change by heat alone, but is readily reduced to the metallic state by heat and combustible matter; and is hence much employed as an oxidizing agent in the analysis of organic substances. It is insoluble in water, and does not affect the vegetable blue colours; it combines with nearly all the acids, forming salts which have a green or blue tint. It is soluble likewise in ammonia, forming with it a deep blue solution, a property by which protoxide of copper is distinguished from all other substances. Its salts are distinguished from most substances by their colour, and are easily recognised by reagents. When pure soda or potassa is mixed with a solution of sulphate of the protoxide, a greenish blue disulphate at first subsides; but as soon as the alkali is added in excess, a blue bulky hydrate of the oxide is formed, which is decomposed by boiling, and consequently becomes black. Pure ammonia also throws down the disulphate when carefully added; but an excess of the alkali instantly redissolves the precipitate, and forms a deep blue solution. Alkaline carbonates cause a bluish-green precipitate, carbonate of the protoxide, which is redissolved by an excess of carbonate of ammonia. It is precipitated as a dark brown sulphuret by hydrosulphuric acid, and as a reddish-brown ferrocyanuret by ferrocyanuret of potassium. It is thrown down of a yellowish-white colour by albumen, and M. Orfila has proved that this compound is inert, so that albumen is an antidote to poisoning by copper.

Copper is separated in the metallic state by a rod of iron or zinc. The copper thus obtained, after being digested in a dilute solution of hydrochloric acid, is almost chemically pure; and iron, as mentioned above, is used in this way for extracting copper on the large scale from the water accumulating in mines. The beautiful process of electrotyping in copper is founded on the property possessed by zinc, when forming part of a galvanic circle, and in contact with diluted sulphuric acid, of reducing copper from a saturated solution of the sulphate of the protoxide, as a dense, firm, metallic mass, not to be distinguished from a rolled plate of the metal.

The best mode of detecting copper, when supposed to be present in mixed fluids, is by hydrosulphuric acid. The sulphuret, after being collected, and heated to redness in order to char organic matters, should be placed on a piece of porcelain, and be digested in a few drops of nitric acid. Sulphate of protoxide of copper is formed, which, when evaporated to dryness, strikes the characteristic deep blue tint on the addition of ammonia; but the most delicate test of black oxide of copper in solution is ferrocyanide of potassium.

Its eq. is 39·6; symb. $Cu + O$, $\dot{Cu}$, or CuO.

Superoxide.—This oxide was prepared by Thenard by the action of peroxide of hydrogen diluted with water on the hydrated black oxide. It suffers spontaneous decomposition under water; but it may be dried *in vacuo* by means of sulphuric acid. When a solution of nitrate of copper is mixed with one of bleaching powder, along with an excess of lime, there is formed a rose-coloured powder, which consists of lime, in combination with an oxide of copper, containing more oxygen than the protoxide. Krüger calls this oxide cupric acid, and Crum has rendered it highly probable that its formula is Cu_2O_3. It has not been obtained in a separate form. It is possible that it may be the same as the superoxide of Thenard, if indeed the latter be not a compound of protoxide of copper and peroxide of hydrogen. The superoxide is supposed by some to be CuO_2, but there is no good evidence of this, and the experiments of Crum, above mentioned, are entirely in favour of the existence of a cupric acid, the eq. of which is 87·2, and its formula Cu_2O_3.

Nituret.—To prepare this compound, protoxide of copper, obtained from the sulphate by potassa at the temperature of ebullition, being well washed and dried, is exposed in a tube to a current of dry ammonia, when it absorbs the gas, heat being disengaged, and is gradually converted into a green powder. If the heat be allowed to rise too high, metallic copper only is left. When no more water is formed, the oxide is found to have been converted into the nituret. It is purified from adhering oxide by digestion with a mixture of aqua ammoniæ and carbonate of ammonia, and dried. It then forms a dark greenish gray powder, which, when heated in the air to 572°, becomes suddenly incandescent, and is resolved into nitrogen gas and metallic copper. The following equation explains its formation: $6CuO + 2NH_3 = Cu_6N + 6HO + N$.

Its eq. is 203·6; symb. $6Cu + N$, or Cu_6N.

Dichloride.—*Prep.*—When copper filings are introduced into an atmosphere of chlorine gas, the metal takes fire spontaneously, and both the chlorides are generated. The *dichloride* may be conveniently prepared by heating copper filings with twice their weight of corrosive sublimate. In this way it was originally made by Boyle, who termed it *resin of copper*, from its resemblance to common resin. Proust, who called it *white muriate of copper*, procured it by the action of protochloride of tin on chloride of copper; and also by decomposing the chloride by heat, air being excluded. It is slowly deposited in crystalline grains when the green solution of chloride of copper is kept in a corked bottle in contact with metallic copper.

Prop.—The dichloride of copper is fusible at a heat just below redness, and bears a red heat in close vessels without subliming. It is insoluble in water, but dissolves in hydrochloric acid, and is precipitated unchanged by water as a white powder. Its colour varies with the mode of preparation, being white, yellow, or dark brown. It is apt to absorb oxygen from the atmosphere, forming a green-coloured compound of oxide and chloride of copper ; a change to which the dichloride prepared in the moist way is peculiarly prone.

Its eq. is 98·62 ; symb. $2Cu + Cl$, or Cu_2Cl.

Chloride.—The chloride of copper is obtained in solution of a green colour by dissolving protoxide of copper in hydrochloric acid, and crystallizes by due concentration in green needles which are deliquescent and very soluble in alcohol. When heated they fuse, lose water, and the anhydrous chloride in form of a yellow powder is left; but the heat must not exceed 400°, as beyond that degree the chloride loses half its chlorine, and is converted into the dichloride.

Its eq. is 66·02 ; symb. $Cu + Cl$, or $CuCl$.

Diniodide of Copper.—This substance is obtained by adding iodide of potassium to a solution made of the sulphates of the protoxides of copper and iron, both in crystals, in the ratio of 1 to $2\frac{1}{4}$, when the protoxide of iron takes the oxygen of the oxide of copper and the iodine the metallic copper, forming a white precipitate, the diniodide. It may be dried, and will bear a high temperature in close vessels, without change ; but if heated with the oxides of iron, manganese, or copper, iodine is expelled and the copper oxidized.

Its eq. is 189·5 ; symb. $2Cu + I$, or Cu_2I.

Iodide of Copper is scarcely known. For on mixing a salt of oxide of copper with iodide of potassium, iodine is set free and the diniodide of copper falls. A small quantity of iodide of copper remains in solution.

Sulphurets of Copper.—The disulphuret is a natural production, well known to mineralogists under the name of *copper glance ;* and in combination with protosulphuret of iron, it is a constituent of variegated copper ore, the chief ore of copper. It is formed artificially by heating copper filings with a third of their weight of sulphur, the combination being attended with such free disengagement of heat, that the mass becomes vividly luminous.

Its eq. is 79·3 ; symb. $2Cu + S$, or Cu_2S.

Sulphuret of Copper is formed by the action of hydrosulphuric acid on a salt of copper. When ignited without exposure to the air, it loses half of its sulphur, and is converted into the disulphuret.

Its eq. is 47·7; symb. $Cu + S$, or CuS.

Phosphurets of Copper.—Rose states that the triphosphuret is generated by the action of phosphuretted hydrogen gas on dichloride of copper, the mutual interchange of elements being such that

3 eq. Dichloride of Copper	$3Cu_2Cl$	yield	2 eq. Triphosphuret	$2Cu_3P$
and 1 eq. Phospuretted Hyd.	P_2H_3		and 3 eq. Hydrochl. Acid	$3HCl$.

The subsesquiphosphuret is formed by a similar interchange between chloride of copper and phosphuretted hydrogen, so that

3 eq. Chloride of Copper	$3CuCl$.	yield	1 eq. Subsesquiphosphuret	Cu_3P_2
and 1 eq. Phosp. Hyd.	P_2H_3		and 3 eq. Hydrochloric Acid	$3HCl$.

Rose obtained the protophosphuret by the action of hydrogen gas on phosphate of protoxide of copper at a red heat. All these phosphurets resemble each other, being pulverulent, of a grey colour, insoluble in hydrochloric acid, oxidized and dissolved by nitric acid, and burn with a phosphorous flame below the blowpipe. A phosphuret of copper is also obtained by transmitting phosphuretted hyhrogen gas through a solution of sulphate of copper; but the dark precipitate which falls seems to be a variable mixture of different phosphurets, phosphoric acid being generated at the same time. (An. de Ch. et Ph. li. 47.) I have given these phosphurets in the form adopted by Rose; but the eq. of phosphorus used by him being only half of that now employed in this work, the formulæ, if the existence of the compounds be confirmed, must be changed accordingly to Cu_6P for the first, Cu_3P for the second, and Cu_2P for the third, or protophosphuret of Rose. Their names would also require to be altered; but in the mean time, in the imperfect state of our knowledge, I have not made these changes.

SECTION XXII.

LEAD.

Hist. and Prep.—This metal was well known to the ancients. As a native production it is very rare; but in combination with sulphur it occurs in great quantity. All the lead of commerce is extracted from the native sulphuret, the *galena* of mineralogists. This ore, in the state of a coarse powder, is heated in a reverberatory furnace; when part of it is oxidized, yielding sulphate of protoxide of lead, sulphuric acid, which is evolved, and free oxide of lead. These oxidized portions then react on sulphuret of lead: by the reaction of 2 eq. of oxide of lead, and one of the sulphuret, 3 eq. of metallic lead and one of sulphurous acid result; while one equivalent of the sulphuret and one of sulphate mutually decompose each other, giving rise to 2 eq. of sulphurous acid and two of metallic lead. The slag which collects on the surface of the fused lead contains a large quantity of sulphate of protoxide of lead, and is decomposed by the addition of quicklime, the oxide so separated reacting as before on sulphuret of lead. The lead of commerce commonly contains silver, iron, and copper.

Prop.—It has a bluish-grey colour, and when recently cut, a strong metallic lustre; but soon tarnishes by exposure to the air, acquiring a superficial coating of carbonate of protoxide of lead. (Christison.) Its sp. gr. is 11·381. It is soft, flexible, and inelastic. It is both malleable and ductile, possessing the former property in particular to a considerable extent. In tenacity, it is inferior to all ductile metals. It fuses at about 612°, and when slowly cooled forms octohedral crystals. It may be heated to whiteness in close vessels without subliming.

Lead absorbs oxygen quickly at high temperatures. When fused in open vessels, a grey film is formed upon its surface, which is a mixture of metallic lead and protoxide; and when strongly heated, it is dissipated in fumes of the protoxide. In distilled water, previously boiled and preserved in close vessels, it undergoes no change; but in open vessels it is oxidized with considerable rapidity, yielding minute, shining, brilliantly white, crystalline scales of carbonate of the protoxide, the oxygen and carbonic acid being derived from the air. The presence of saline matter in water retards the oxidation of the lead; and some salts, even in very minute quantity, prevent it altogether. The protecting influence, exerted by certain substances, was first noticed by Guyton Morveau; but it has been minutely investigated by Christison of Edinburgh, who has discussed the subject in his excellent Treatise on Poisons. He finds that the preservative power of neutral salts is materially connected with the insolubility of the compound which their acid is capable of forming with lead. Thus, phosphates and sulphates, as well as chlorides and iodides, are highly preservative; so small a quantity as 1-30,000th part of phosphate of soda or iodide of potassium in distilled water preventing the corrosion of lead. In a preservative solution the metal gains weight during some weeks, in consequence of its surface gradually acquiring a superficial coating of carbonate, which is slowly decomposed by the saline matter of the solution. The metallic surface being thus covered with an insoluble film, which adheres tenaciously, all further change ceases. Many kinds of spring water, owing to the salts which they contain, do not corrode lead; and hence, though intended for drinking, it may be safely collected in leaden cisterns. Of this, the water of Edinburgh is a remarkable instance. Although soft, not containing more than 5 or 6 grains per gallon of earthy, saline, and organic matters, it does not become at all impregnated with lead in leaden pipes or cisterns.

Lead is not attacked by the hydrochloric or the vegetable acids, though their presence, at least in some instances, accelerates the absorption of oxygen from the atmosphere in the same manner as with copper. Cold sulphuric acid does not act upon it; but when boiled in that liquid, the lead is slowly oxidized at the expense of the acid. The only proper solvent for lead is nitric acid. This reagent oxidizes it rapidly, and forms with its oxide a salt which crystallizes in opaque octohedrons by evaporation.

From my experiments on the composition of the protoxide of lead, and of the nitrate and sulphate of that oxide, I have deduced 103·6 as the eq., a number which agrees very closely with the researches of Berzelius on the same subject. (Phil. Trans. 1833, part ii.) Its symb. is Pb. The composition of its compounds described in this section is as follows:—

	Lead.			Equiv.	Formulæ.
Dinoxide .	207·2	2 eq.+Oxygen .	8	1 eq.=215·2	$2Pb+O$ or Pb_2O.
Protoxide .	103·6	1 eq.+ . . .	8	1 eq.=111·6	$Pb+O$ or PbO.
Sesquioxide	207·2	2 eq.+ . . .	24	3 eq.=321·2	$2Pb+3O$ or Pb_2O_3.
Peroxide .	103·6	1 eq.+ . . .	16	2 eq.=119·6	$Pb+2O$ or PbO_2.
Red Oxide	310·8	3 eq.+ . . .	32	4 eq. } =342·8	$3Pb+4O$.
	or Protox. 223·2	or 2 eq.+Perox.	119·6	1 eq. }	$2PbO+PbO_2$.
Chloride .	103·6	1 eq.+Chlorine	35·42	1 eq.=139·02	$Pb+Cl$.
Iodide . .	103·6	1 eq.+Iodine .	126·3	1 eq.=229·9	$Pb+I$.
Bromide .	103·6	1 eq.+Bromine	78·4	1 eq.=182	$Pb+Br$.
Fluoride .	103·6	1 eq.+Fluorine	18·68	1 eq.=122·28	$Pb+F$.
Sulphuret .	103·6	1 eq.+Sulphur	16·1	1 eq.=119.7	$Pb+S$.
Phosphuret Carburet	Composition uncertain.				

Dinoxide of Lead.—Dulong observed that on heating dry oxalate of protoxide of lead in a glass tube to low redness, air being excluded, a mixture of carbonic acid and carbonic oxide gases is evolved, and a suboxide remains of a dark grey, nearly black, colour. Boussingault has lately proved that it is a dinoxide. It does not unite with acids, but is resolved by them into a salt of the protoxide with separation of metallic lead. (An. de Ch. et Ph. liv. 263.)

Its eq. is 215·2; symb, $2Pb + O$, or Pb_2O.

Protoxide.—*Prep.*—This oxide is prepared on a large scale by collecting the grey film which forms on the surface of melted lead, and exposing it to heat and air until it acquires a uniform yellow colour. In this state it is the *massicot* of commerce; and when partially fused by heat, the term *litharge* is applied to it. As thus procured it is always mixed with the red oxide. It may be obtained pure by adding ammonia to a cold solution of nitrate of protoxide of lead until it is faintly alkaline, washing the precipitated subnitrate with cold water, and when dry, heating it to moderate redness for an hour in a platinum crucible. An open fire should be used, and great care taken to prevent combustible matter in any form from contact with the oxide.

Prop.—It is red while hot, but has a rich lemon-yellow colour when cold, is insoluble in water, fuses at a bright red heat, and is fixed and unchangeable in the fire. Its sp. gr. is 9·4214. The fused protoxide has a highly foliated texture, and is very tough, so as to be pulverized with difficulty. By transmitted light it is yellow; but by reflected light it appears green in some parts and yellow in others. Heated with combustible matters it parts with oxygen, and is reduced. From its insolubility it does not change the vegetable colours under common circumstances; but when rendered soluble by a small quantity of acetic acid, it has a distinct alkaline reaction. It unites with acids, and is the base of all the salts of lead, most of which are of a white colour. From its solutions it is precipitated by pure alkalies as a white hydrate, which is redissolved by potassa in excess; as a white carbonate, which is the well-known pigment *white lead*, by alkaline carbonates; as a white sulphate by soluble sulphates; as a dark brown sulphuret by hydrosulphuric acid; and as yellow iodide of lead by hydriodic acid or iodide of potassium.

With regard to the poisonous property of the salts of lead, a remarkable fact has been observed by my colleague Dr. A. T. Thomson, who has proved that of all the ordinary preparations of lead, the carbonate is by far the most virulent poison. Any salt of lead which is easily convertible into the carbonate, as for instance the subacetate, is also poisonous; but he has given large doses of the nitrate of the protoxide and of the chloride of lead to rabbits without producing perceptible inconvenience. He finds that acetate of protoxide of lead, mixed with vinegar to prevent the formation of any carbonate, may be freely and safely administered in medical practice.

The best method of detecting the presence of lead in wine or other suspected mixed fluids is by means of hydrosulphuric acid. The sulphuret of lead, after being collected on a filter and washed, is to be digested in nitric acid diluted with twice its weight of water, until the dark colour of the sulphuret disappears. The solution of the nitrate should then be brought to perfect dryness on a watch-glass, in order to expel the excess of nitric acid, and the residue be redissolved in a small quantity of cold water. On dropping a particle of iodide of potassium into a portion of this liquid, yellow iodide of lead will instantly appear.

Protoxide of lead unites readily with earthy substances, forming with them a transparent colourless glass. Owing to this property it is much employed for glazing earthenware and porcelain. It enters in large quantity into the composition of flint glass, which it renders more fusible, transparent, and uniform.

Lead is separated from its salts in a metallic state by iron or zinc. The best way of demonstrating this fact is by dissolving 1 part of acetate of protoxide of lead in 24 of water, and suspending a piece of zinc in the solution by means of a thread. The lead is deposited upon the zinc in a peculiar arborescent form, giving rise to the appearance called *arbor saturni.*

Its eq. is 111·6; symb. $Pb + O$, $\dot{Pb}$, or PbO.

Red Oxide.—Prep.—This compound, the *minium* of commerce, is employed as a pigment, and in the manufacture of flint glass. It is formed by oxidizing lead by heat and air without allowing it to fuse, and then exposing it in open vessels to a temperature of 600° or 700°, while a current of air plays upon its surface. It slowly absorbs oxygen and is converted into minium.

Prop.—This oxide does not unite with acids. When heated to redness it gives off pure oxygen gas, and is reconverted into the protoxide. When digested in nitric acid it is resolved into protoxide and peroxide of lead, the former of which unites with the acid, while the latter remains as an insoluble powder. From the facility with which this change is effected even by acetic acid, most chemists consider red lead, not so much as a definite compound of lead and oxygen, but as a salt composed of the protoxide and peroxide, as above stated. This oxide has been long considered as a sesquioxide, an error first corrected by Dalton (New System of Chemistry, ii. 41), whose observation has been confirmed by Dumas and Philips. (An. de Ch. et Ph. xlix. 398, and Phil. Mag. N.S. iii. 125.) Dumas shows that the minium is not uniform in composition, but consists of variable mixtures of the protoxide with real red lead. The former may be oxidized by continued exposure to air and heat, and may be dissolved by acetic acid very much diluted with cold water.

Its eq. is 342·8; symb. $2PbO + PbO_2$.

Sesquioxide.—Winkelblech (Ann. der Pharm. xxi. 29) has proved the existence of this compound. It is prepared by adding hypochlorite of soda to a solution of protoxide of lead in caustic potash. It forms a reddish-yellow insoluble powder, which is resolved by heat and by acids into protoxide and oxygen. Its eq. is 231·2; symb.

Pb_2O_3. Red lead may be a compound of 1 at. sesquioxide and 1 at. protoxide, Pb_2O_3, $PbO = Pb_3O_4$.

Peroxide.—Prep.—This oxide may be obtained by the action of nitric acid on minium, as just mentioned; by fusing protoxide of lead with chlorate of potassa, at a temperature short of redness, and removing the chloride of potassium by solution in water; and by transmitting a current of chlorine gas through a solution of acetate of the protoxide of lead. In the last the reaction is such, that

1 eq. Chlorine and	2 eq. Protox. Lead	yield	1 eq. Perox. Lead and	1 eq. Chloride Lead
Cl	$2PbO$		PbO_2	$PbCl$.

The chloride is removed by washing with warm water.

Prop.—It is of a puce colour, is insoluble in water, and is resolved by strong ox-acids, such as the sulphuric and nitric, into a salt of the protoxide and oxygen gas. With hydrochloric acid it yields chlorine gas and chloride of lead. At a red heat it emits oxygen gas and is converted into the protoxide.

Its eq. is 119·6; symb. $Pb + 2O$, PbO_2.

Chloride of Lead.—This compound, sometimes called *horn lead*, is slowly formed by the action of chlorine gas on thin plates of lead, and may be obtained more easily by adding hydrochloric acid or a solution of sea-salt to acetate or nitrate of oxide of lead dissolved in water. This chloride dissolves to a considerable extent in hot water, especially when acidulated with hydrochloric acid, and separates on cooling in small acicular anhydrous crystals of a white colour. It fuses at a temperature below redness, and forms as it cools a semi-transparent mass, which has a density of 5·133. It bears a full red heat in close vessels without subliming; but in open vessels it smokes from spurious evaporation, loses some of its chlorine and absorbs oxygen, yielding an oxychloride of a yellow colour.

Its eq. is 139·02; symb. $Pb + Cl$, or $PbCl$.

Iodide of Lead is easily formed by mixing a solution of hydriodic acid in excess with the nitrate of protoxide of lead dissolved in water; and it is of a rich yellow colour. It is dissolved by boiling water, forming a colourless solution, and is deposited on cooling in yellow crystalline scales of a brilliant golden metallic lustre.

Its eq. is 229·9; symb. $Pb + I$, or PbI.

Bromide of Lead.—It falls as a white crystalline powder, of sparing solubility in water, when a soluble salt of lead is mixed with bromide of potassium in solution. Exposed to heat, it fuses into a red liquid which becomes yellow when cold.

Its eq. is 182; symb. $Pb + Br$, or Pb,Br.

Fluoride of Lead is formed by mixing hydrofluoric acid with acetate of protoxide of lead, and falls as an uncrystalline white powder of very sparing solubility. It is soluble in nitric and hydrochloric acids, but is decomposed when the solution is evaporated.

Its eq. is 122·28; symb. $Pb + F$, or PbF.

Sulphurets of Lead.—It is probable that lead unites with sulphur in several different proportions; but the only one of these compounds well known to chemists is the native sulphuret, *galena*, which occurs in cubic crystals, or in forms allied to the cube, and is the ore from which all the lead of commerce is obtained. It may be formed artificially by fusing lead with sulphur, or by the action of hydrosulphuric acid on a salt of lead.

Its eq. is 119·7; symb. $Pb + S$, or PBS.

Phosphuret of Lead has been little examined. It may be formed by heating phosphate of oxide of lead with charcoal, by mixing a solution of phosphorus in alcohol or ether with the solution of a salt of lead, or by the action of phosphuretted hydrogen on a similar solution.

Carburet of Lead may be obtained by reducing oxide of lead in a state of fine division and intimate admixture with charcoal. It is also generated when salts of lead, which contain a vegetable acid, are decomposed by heat in close vessels. (Berzelius.)

ORDER III.

METALS, THE OXIDES OF WHICH ARE REDUCED TO THE METALLIC STATE BY RED HEAT.

SECTION XXIII.

MERCURY OR QUICKSILVER.

Hist. and Prep.—This metal was well known to the ancients. The principal mines from which it is obtained are those of Idria in Carniola and Almaden in Spain, where it is found both in the native state and combined with sulphur as cinnabar, the latter being the most abundant. From this ore the metal is extracted by heating it with lime or iron filings, by which means the mercury is volatilized and the sulphur retained. As prepared on a large scale it is usually mixed in small quantity with other metals, from which it may be purified by cautious distillation.

Prop.—Distinguished from all other metals by being fluid at common temperatures. It has a tin-white colour and strong metallic lustre. It becomes solid at a temperature which is 39 or 40 degrees below zero; and in congealing, it evinces a strong tendency to crystallize in octohedrons. It contracts greatly at the moment of congelation; for while its density at 47° is 13·545, that of frozen mercury is 15·612. When solid it is malleable, and may be cut with a knife. At 620°, or near that degree, it enters into ebullition, and condenses again on cool surfaces into metallic globules.

Mercury, if quite pure, is not tarnished in the cold by exposure to air and moisture; but if it contain other metals, the amalgam of those metals oxidizes readily, and collects as a film upon its surface. It is said to be oxidized by long agitation in a bottle half full of air, and the oxide so formed was called by Boerhaave *Ethiops per se;* but it is very probable that the oxidation of mercury observed under these circumstances was solely owing to the presence of other metals. When exposed to air or oxygen gas, while in the form of vapour, it slowly absorbs oxogen, and is converted into peroxide of mercury.

The only acids that act on mercury are the sulphuric and nitric acids. The former has no action whatever in the cold; but on the application of heat, the mercury is oxidized at the expense of the acid, pure sulphurous acid gas is disengaged, and a sulphate of mercury is generated. Nitric acid acts energetically upon mercury both with and without the aid of heat, oxidizing and dissolving it with evolution of peroxide of nitrogen.

From some late analyses on the peroxide and chlorides of mercury, I have inferred that its equivalent is 202 (Phil. Trans. 1833, part ii.); its symb. is Hg. The composition of its compounds described in this section is as follows:

	Mercury.			Equiv.	Formulæ.
Protoxide	202	1 eq.+Oxygen	8	1 eq.=210	$Hg+O$ or HgO.
Peroxide	202	1 eq.+ do.	16	2 eq.=218	$Hg+2O$ or $HgO._2$.
Nituret	606	3 eq.+Nitrogen	28	2 eq.=634	$3H+2N$ or Hg_3N_2.
Protochloride	202	1 eq.+Chlorine	35·42	1 eq.=237·42	$Hg+Cl$ or $HgCl$.
Bichloride	202	1 eq.+ do.	70·84	2 eq.=272·84	$Hg+2Cl$ or $HgCl_2$.
Iodide	202	1 eq.+Iodine	126·3	1 eq.=328·3	$Hg+I$ or HgI.
Sesquiodide	404	2 eq.+ do.	378·9	3 eq.=782·9	$2Hg+3I$ or Hg_2I_2.
Biniodide	202	1 eq.+ do.	252·6	2 eq.=454·6	$Hg+2I$ or HgI_2.
Protobromide	202	1 eq.+Bromine	78·4	1 eq.=280·4	$Hg+Br$ or $HgBr$.
Bibromide	202	1 eq.+ do.	156·8	2 eq.=358·8	$Hg+2Br$ or $HgBr_2$.
Protosulphuret	202	1 eq.+Sulphur	16·1	1 eq.=218·1	$Hg+S$ or HgS.
Bisulphuret	202	1 eq.+ do.	32·2	2 eq.=234·2	$Hg+2S$ or HgS_2.
Ioduretted bichloride of Mercury		$HgCl_2$	5456·8	20 eq. =5583·1	$20HgCl_2+I$.
		I	126·3	1 eq.	
Iodo-bichloride of Mercury		$HgCl_2$	10913·6	40 eq. =11368·2	$40HgCl_2+HgI_2$.
		HgI_2	454·6	1 eq.	

On the continent the eq. of mercury is taken at 101, and consequently what is here called the protoxide becomes a suboxide Hg_2O, while the peroxide becomes protoxide HgO, and its eq. 109 instead of 218. The same modifications apply to all the compounds in the table, if we adopt the smaller eq. of mercury. I am not aware what the reasons are, which induce the continental chemists to do so; and I have therefore retained the eq. formerly adopted in this work. The difference, however, must be borne in mind in reading foreign works.

Protoxide.—Prep.—Best by the process recommended by Donovan (An. of Phil. xiv.): this consists in mixing calomel briskly in a mortar with pure potassa in excess, so as to effect its decomposition as rapidly as possible; the protoxide is then washed with cold water, and dried spontaneously in a dark place. These precautions are rendered necessary by the tendency of the protoxide to resolve itself into the peroxide and metallic mercury, a change which is easily effected by heat, by the direct solar rays, and even by daylight. It is on this account very difficult to procure protoxide of mercury in a state of absolute purity.

Prop.—A black powder, which is exceedingly prone to decomposition, is insoluble in water, unites with acids, but is a weak alkaline base. It is precipitated from a solution of its salts, of which the nitrate is the most interesting, as the black protoxide by pure alkalies; as a white carbonate, which soon becomes dark from the loss of carbonic acid, by alkaline carbonates; as calomel by hydrochloric acid or any soluble chloride; and as the black protosulphuret by hydrosulphuric acid. Of these tests, the action of hydrochloric acid is the most characteristic. The oxide is reduced to the metallic state by copper, phosphorous acid, or protochloride of tin.

Its eq. is 210; symb. $Hg + O$, $\dot{Hg}$, or HgO.

Peroxide.—Prep.—Either by the combined agency of heat and air, as already mentioned, or by dissolving mercury in nitric acid, and exposing the nitrate so formed to a temperature just sufficient for expelling the whole of the nitric acid. It is commonly known by the name of *red precipitate*. The peroxide prepared from the nitrate almost always contains a trace of nitric acid, which may be detected by heating it in a clean glass tube by means of a spirit-lamp: a yellow ring, formed of subnitrate of oxide of mercury, collects within the tube just above the part which is heated. (Clark.) This impurity is easily got rid of by cautiously heating the impure oxide in a porcelain crucible over the spirit-lamp, until mercury begins to be given off, and is deposited on a cold surface held close to the crucible.

As thus prepared, it is commonly in the form of shining crystalline scales of a nearly black colour while hot, but red when cold: when very finely levigated, the peroxide has an orange colour. It is said to be soluble to a small extent in water, forming a solution which has an acrid metallic taste, and communicates a green colour to the blue infusion of violets, but this property most likely depends on the presence of a trace of subnitrate, as above described. When heated to redness, it is converted into metallic mercury and oxygen. Long exposure to light has a similar effect. (Guibourt.)

Some of the neutral salts of this oxide, such as the nitrate and sulphate, are converted by water, especially at a boiling temperature, into insoluble yellow subsalts, leaving a strongly acid solution, in which a little of the original salt is dissolved. This oxide is separated from all acids as a yellow hydrate, by the pure fixed alkalies. Carbonate of potash or soda causes a dirty brownish red precipitate. Ammonia and its carbonate causes a white precipitate, which is a double salt, consisting of one equivalent of the acid, one equivalent of the peroxide, and one equivalent of ammonia. The oxide is readily reduced to the metallic state by metallic copper. Hydrosulphuric acid, phosphorous acid, and protochloride of tin, reduce the peroxide into the protoxide; and when added in larger quantity, the first throws down a black sulphuret, and the two latter metallic mercury. The action of hydrosulphuric acid on a solution of corrosive sublimate is, however, peculiar; for at first it occasions a white precipitate which, according to Rose, is a compound of two equivalents of bisulphuret to one of bichloride of mercury. This gas acts on bibromide and biniodide of mercury in a similar manner. (An. de Ch. et Ph. xl. 46.)

Its eq. is 218; symb. $Hg + 2O$, $\ddot{Hg}$, or HgO_2.

Nituret of Mercury.— When precipitated and well-washed and dried peroxide of mercury is placed in a tube, and a current of dry ammonia passed over it till it is saturated, and the tube then heated to 302°, the current of gas being continued, as long as water is formed, there is obtained a flea-brown powder, which is a compound of mercury with nitrogen. Its formation is thus explained: $3HgO_2 + 2NH_3 = Hg_3N_2 + 6HO$. It explodes with fearful violence, shattering the vessels employed, when heated, or by friction and percussion. (Plantamour.)

Its eq. is 634; symb. $3Hg + 2N$ or Hg_3N_2.

Protochloride.—Prep.—Syn. Subchloride.—Protochloride of mercury, or *calomel*, is a rare mineral production, called horn quicksilver, which occurs crystallized in quadrangular prisms terminated by pyramids. It is always generated when chlorine comes in contact with mercury at common temperatures; and also by the contact of metallic mercury and the bichloride at a high temperature. It may be made by precipitation, by mixing nitrate of protoxide of mercury in solution with hydrochloric acid or any soluble chloride. It is more commonly prepared by sublimation. This is conveniently done by triturating 272·84 parts or 1 eq. of the bichloride with 202 parts or 1 eq. of mercury, until the metallic globules entirely disappear, and then subliming. When first prepared it is always mixed with some corrosive sublimate, and therefore should be reduced to powder and well washed before being employed for chemical or medical purposes.

Prop.—When obtained by sublimation it is in semi-transparent crystalline cakes; but as formed by precipitation, it is a white powder. Its sp. gr. is 7·2. At a heat short of redness, but higher than the subliming point of the bichloride, it rises in vapour without previous fusion; but during the sublimation a portion is always resolved into mercury and the bichloride. It is yellow while warm, but recovers its whiteness on cooling. It is distinguished from the bichloride by not being poisonous, by having no taste, and by being exceedingly insoluble in water. Acids have little effect upon it; but pure alkalies decompose it, separating the black protoxide of mercury. When calomel is boiled in a solution of hydrochlorate of ammonia, it is converted into corrosive sublimate and metallic mercury. Chloride of sodium has a similar effect, though in a less degree.

Its eq. is 237·42; symb. $Hg + Cl$, or $HgCl$.

Bichloride.—Prep.—When mercury is heated in chlorine gas, it takes fire, and burns with a pale red flame, forming the well-known medicinal preparation and virulent poison *corrosive sublimate* or bichloride of mercury. It is prepared for medical purposes by subliming a mixture of bisulphate of the peroxide of mercury with chloride of sodium or sea-salt. The exact quantities required for mutual decomposition are 298·2 parts or 1 eq. of the bisulphate, to 117·44 parts or 2 eq. of the chloride. Thus,

Bisulphate of Mercury		1 eq.	Chloride of Sodium.		2 eq.
Sulphuric Acid .	80·2 or 2 eq.	$2SO_3$.	Chlorine .	70·84 or 2 eq.	2 Cl.
Peroxide of Mer. .	218 or 1 eq.	HgO_2.	Sodium .	46·6 or 2 eq.	2 Na.
	298·2	HgO_2+2SO_3.		117·44	2 NaCl.

And by mutual interchange of elements they produce

Bichloride of Mercury		1 eq.	Sulphate of Soda		2 eq.
Mercury .	202 or 1 eq.	. Hg.	Soda . . .	62·6 or 2 eq. .	2NaO.
Chlorine .	70·84 or 2 eq.	. 2Cl.	Sulphuric Ac. .	80·2 or 2 eq. .	$2SO_3$.
	272·84	$HgCl_2$.		142·8	$2NaO,SO_3$.

The products have exactly the same weight (272·84 + 142·8 =

415·64) as the compounds (298·2 + 117·44 = 415·64) from which they were prepared.

Prop.—When obtained by sublimation, it is a semi-transparent colourless substance, of a crystalline texture. It has an acrid, burning taste, and leaves a nauseous metallic flavour on the tongue. Its sp. gr. is 5·2. When exposed to a heat short of incandescence, it is fused, enters into ebullition from the rapid formation of vapour, and is deposited without further change on cool surfaces as a white crystalline sublimate. It requires twenty times its weight of cold, and only twice its weight of boiling water for solution, and is deposited from the latter, as it cools, in the form of prismatic crystals. Strong alcohol and ether dissolve it in the same proportion as boiling water; and it is soluble in half its weight of concentrated hydrochloric acid at the temperature of 70°. With the chlorides of potassium and sodium, hydrochlorate of ammonia, and several other bases, it enters into combination, forming double salts, which are more soluble than the chloride itself. When its solution in water is agitated with ether, the latter abstracts the bichloride, and rises with it to the surface of the former, thus affording strong evidence of the bichloride having existed as such in the water. Its aqueous solution is gradually decomposed by light, calomel being deposited.

The pure and carbonated fixed alkalies throw down the hydrated peroxide of mercury, from a solution of corrosive sublimate. Ammonia, on the contrary, causes the deposition of a white matter, which is commonly known under the name of the white precipitate. This substance has been recently examined by Kane. (Trans. Irish Academy, xvii.) He finds that on adding a slight excess of ammonia just one half of the chlorine of the corrosive sublimate falls, the other half remaining in the solution with ammonia. The precipitate nevertheless does not contain calomel, as is proved by its complete solubility in hydrochloric and nitric acids. From his analysis it is composed of

Mercury . . .	78·6	Ammonia	6·77
Chlorine . . .	13·85	Hygrometric water, loss, and oxygen	0·78

Its atomic constitution would appear from this analysis to contain the compound radical which is the base of the amides, and its formula is believed to be $HgCl_2 + HgAd_2$ ($Ad = NH_2$ or amide). By the action of boiling water, it loses half its chlorine and ammonia, peroxide of mercury being at the same time formed, and a canary-yellow powder is produced. Kane finds that on treating calomel with ammonia, it, too, loses only one half its chlorine, and a compound analogous to white precipitate is obtained.

The presence of mercury in a fluid supposed to contain corrosive sublimate, may be detected by concentrating and digesting it with an excess of pure potassa. Oxide of mercury, which subsides, is then sublimed in a small glass tube by means of a spirit-lamp, and obtained in the form of metallic globules. But in cases of poisoning, when the bichloride is mixed with organic substances, Christison recommends that the liquid, without previous filtration, be agitated with a fourth of its volume of ether, which separates the poison from the aqueous part, and rises to the surface. The ethereal solution is then evaporated on a watch glass, the residue dissolved in hot water, and the mercury precipitated in the metallic state by protochloride of tin at a boiling temperature, If, as is probable, most of the poison is already converted into calomel, and thereby rendered insoluble, as many vegetable fibres should be picked out as possible, and the whole at once digested with protochloride of tin. The organic substances are then dissolved in a hot solution of caustic potassa, and the insoluble parts washed and sublimed to separate the mercury. (Christison on Poisons.)

A very elegant method of detecting the presence of mercury is to place a drop of the suspected liquid on polished gold, and to touch the moistened surface with a piece of iron wire or the point of a penknife, when the part touched instantly becomes white, owing to the formation of an amalgam of gold. This process was originally suggested by Sylvester, and has since been simplified by Paris. (Medical Jurisprudence, by Paris and Fonblanque.)

Many animal and vegetable solutions convert bichloride of mercury into calomel, a portion of hydrochloric acid being set free at the same time. Some substances effect this change slowly; while others, and especially albumen, produce it in an instant. Thus, when a solution of corrosive sublimate is mixed with albumen, a white flocculent precipitate subsides, which Orfila has shown to be a compound of calomel and albumen, and which he has proved experimentally to be inert. (Toxicologie, vol. i.) Consequently, a solution of the white of eggs is an antidote to poisoning by corrosive sublimate. The muscular and membranous parts, even of a living animal, produce a similar effect; and the causticity of corrosive sublimate seems owing to the destruction of the animal fibre, by which the decomposition of the bichloride is accompanied, and which constitutes an essential part of the chemical change. Its eq. is 272·84; symb. $Hg + 2Cl$, or $HgCl_2$.

Protiodide of Mercury.—This compound is obtained by mixing nitrate of protoxide of mercury in solution with iodide of potassium. It is a green powder insoluble in water, and disposed to resolve itself under the influence of heat or solar light into mercury and the biniodide. However, when the heat is quickly supplied, it is fused and sublimed without material change.

Its eq. is 328·3; symb. Hg + I, or HgI.

Sesquiiodide.—This compound falls as a yellow powder when iodide of potassium is added in solution to the mixed nitrates of the protoxide and peroxide of mercury, the latter being in excess. The precipitate is digested with a solution of sea-salt, which takes up any biniodide which may have fallen.

Its eq. is 782·9; symb. 2Hg + 3I, or Hg_2I_3.

Biniodide.—This compound is formed by mixing nitrate of the peroxide or bichloride of mercury with iodide of potassium in solution, and falls as a rich red-coloured powder of a tint which surpasses in beauty that of vermilion, though the colour is said to be less permanent. Though insoluble in water, it dissolves freely in an excess of either of its precipitants. If taken up in a hot solution of nitrate of peroxide of mercury, the biniodide crystallizes out on cooling in scales of a beautiful red tint. The same crystals separate from a solution in iodide of potassium; but if the liquid be concentrated, a double iodide of mercury and potassium subsides.

The biniodide, when exposed to a moderate heat, gradually becomes yellow; and the particles, though previously in powder, acquire a crystalline appearance. At about 400° it forms a yellow liquid, which slowly sublimes in small transparent scales, or in large rhombic tables, when a considerable quantity is sublimed. The crystals retain their yellow colour at 60° if kept very tranquil; but if the temperature be below a certain point, or they are rubbed or touched, they quickly become red. This phenomenon is entirely due to a change in molecular arrangement; and under the microscope the particles are seen to be in motion during the change: the different colours so often witnessed in the same substances at different temperatures, as in peroxide of mercury and the protoxides of lead and zinc, appear to be phenomena of the same nature. Its eq. is 454·6; symb. Hg + 2I, or HgI_2.

Ioduretted Bichloride of Mercury.—This compound has recently been described by Lassaigne. (An. de Ch. et Ph. lxiii. 106.) It is formed by adding to an alcoholic solution of iodine a solution of corrosive sublimate, when the deep colour of the iodine gradually disappears, and a colourless solution is obtained. It is remarkable, that in this combination the iodine cannot be detected by starch and chlorine or sulphurous acid, as in its other combinations. The compound is decomposed by heat, but may be obtained in crystals by evaporating a concentrated solution at a moderate temperature.

Its eq. is 5583·1; symb. $20HgCl_2 + I$.

Iodo-bichloride of Mercury.—This compound was described by Boullay. (An. de Ch. et Ph. xxxvi. 366.) It is formed by dissolving biniodide of mercury in corrosive sublimate, when a colourless crystalline compound is obtained. It is composed of 40 eq. of the bichloride and 1 of the biniodide.

Its eq. is 11368·2; symb. $40HgCl_2 + HgI_2$.

Protobromide of Mercury.—It is precipitated as a white insoluble powder by mixing nitrate of protoxide of mercury with bromide of potassium. Its eq. is 280·4; symb. $Hg + Br$, or $HgBr$.

The bibromide is a white crystallizable compound, soluble in water and alcohol, fusible and volatile, and in many respects analogous to the bichloride. It is formed by acting on peroxide of mercury with hydrobromic acid, or digesting the preceding compound with bromine.

Its eq. is 358·8; symb. $Hg + 2Br$, or $HgBr_2$.

Sulphurets of Mercury.—The protosulphuret may be prepared by transmitting a current of hydrosulphuric acid gas through a dilute solution of nitrate of protoxide of mercury, or through water in which calomel is suspended. It is a black-coloured substance, which is oxidized by digestion in strong nitric acid. When exposed to heat it is resolved into the bisulphuret and metallic mercury.

Its eq. is 218·1; symb. $Hg + S$, or HgS.

The bisulphuret is formed by fusing sulphur with about six times its weight of mercury, and subliming in close vessels. When procured by this process it has a red colour, and is known by the name of *factitious cinnabar.* Its tint is greatly improved by being reduced to powder, in which state it forms the beautiful pigment *vermilion.* It may be obtained in the moist way by pouring a solution of corrosive sublimate into an excess of hydrosulphate of ammonia. A black precipitate subsides, which acquires the usual red colour of cinnabar when sublimed. The black precipitate formed by the action of hydrosulphuric acid on bicyanuret of mercury, is likewise a bisulphuret. Cinnabar, as already mentioned, occurs native.

When equal parts of sulphur and mercury are triturated together until metallic globules cease to be visible, the dark-coloured mass called *Ethiops mineral* results, which Mr. Brande has proved to be a mixture of sulphur and bisulphuret of mercury. (Journal of Science, vol. xviii. p. 294.)

Cinnabar is not attacked by alkalies, or any simple acid; but it is dissolved by the nitro-hydrochloric, with formation of sulphuric acid and peroxide of mercury.

Its eq. is 234·2; symb. $Hg + 2S$, or HgS_2.

SECTION XXIV.

SILVER.

Hist.—THIS metal was known to the ancients. It frequently occurs native in silver mines, both massive and in octohedral or cubic crystals. It is also found in combination with gold, tellurium, antimony, copper, arsenic, and sulphur. In the state of sulphuret it so frequently accompanies galena, that the lead of commerce is rarely quite free from traces of silver.

Prep.—Silver is extracted from its ores by two processes which are essentially distinct; one of them being contrived to separate it from lead, the other, the process by *amalgamation*, being especially adapted to those ores which are free from lead. The principle of its separation from lead is founded on the different oxidability of lead and silver, and on the ready fusibility of litharge. The lead obtained from those kinds of galena which are rich in sulphuret of silver is kept at a red heat in a flat furnace, with a draught of air constantly playing on its surface; the lead is thus rapidly oxidized; and as the oxide, at the moment of its formation, is fused, and runs off through an aperture in the side of the furnace, the production of litharge goes on uninterruptedly until all the lead is removed. The button of silver is again fused in a smaller furnace, resting on a porous earthen dish, made with lixiviated wood-ashes, called a *test*, the porosity of which is so great, that it absorbs any remaining portions of litharge which may be formed on the silver.

Mr. Pattinson of Newcastle has taken out a patent for a new and ingenious process, whereby the extraction of silver from lead is much facilitated. The lead is melted and allowed to cool slowly. The crystals which form first are lead, nearly free from silver. They are removed by means of a perforated ladle, and the process is repeated both with them and with the residue, till there is obtained, on the one hand, lead almost free of silver, while on the other, the whole silver is collected in combination with a small part of the lead, in the fluid residue. This mixture is then subjected to cupellation, which from its smaller bulk is more easily and rapidly accomplished.

The ores commonly employed in the process of amalgamation, which has been long used at Freyberg in Saxony, and is extensively practised in the silver and gold mines of South America, are native silver and its sulphuret. At Freyberg the ore in fine powder is mixed with sea-salt, and carefully roasted in a reverberatory furnace. The production of sulphuric acid leads to the formation of sulphate of soda, while the chlorine of the sea-salt combines with silver. The roasted mass is ground to a fine powder, and, together with mercury, water, and fragments of iron, is put into barrels, which are made to revolve by machinery. In this operation, intended to ensure perfect contact between the materials, chloride of silver is decomposed by the iron, the silver unites with the mercury, and the chloride of iron is dissolved by the water. The mercury is then squeezed through leathern bags, the pores of which permit pure mercury to pass, but retain the amalgam of silver. The combined mercury is then distilled off in close vessels, and the metals obtained in a separate state.

Goldsmiths' silver commonly contains copper and traces of gold, the latter appearing in dark flocks when the metal is dissolved in nitric acid. It may be obtained pure for chemical uses by placing a clean piece of copper in a solution of nitrate of oxide of silver, washing the precipitate with pure water, and then digesting it in ammonia, in order to remove any adhering copper. A better process is to decompose chloride of silver by means of carbonate of potassa. For this purpose precipitate a solution of nitrate of oxide of silver with chloride of sodium, wash the precipitate with water, and dry it. Then put twice its weight of carbonate of potassa into a clean hessian or black-lead crucible, heat it to redness, and throw the chloride by successive portions into the fused alkali. Effervescence takes place from the evolution of carbonic acid and oxygen gases, chloride of potassium is generated, and metallic silver subsides to the bottom. But this process is apt to fail, except in very experienced hands ; for if the heat be too strong, the crucible is rapidly corroded by the fused alkaline mass, and the silver runs into the fire-place or among the fuel ; and if the heat be insufficient, the reduced silver is disseminated through the mass in the form of small globules, and does not collect in a button, because the alkaline mass is not perfectly melted. Even when the process succeeds, and a good button of silver is obtained, some part of the metal is generally found in the globules on the side of the crucible, having been thrown up by the violent effervescence. To avoid these difficulties, Gregory recommends to boil the freshly precipitated and moist chloride with aqua potassæ of sp. gr. 1·25, or 1·3, till it becomes black, by which means it is almost entirely converted into oxide of silver. The black powder being washed and dried, is to be heated with a little carbonate of potash, to reduce the chloride which has not been decomposed. The oxide loses its oxygen, and the whole silver is easily obtained in a button. There is very little effervesence because there is little chloride to be reduced, and the addition of a little borax renders the flux so fusible that the crucible is not endangered. The pure metal may be granulated by pouring it while fused from a height of seven or eight feet into a vessel of water.

Prop.—It has the clearest white colour of all the metals, and is susceptible of receiving a lustre surpassed only by polished steel. In malleability and ductility it is inferior only to gold, and its tenacity is considerable. It is very soft when pure, so that it may be cut with a knife. Its density after being hammered is 10·51. At a full red heat, corresponding to 1873° F. according to Daniell, it enters into fusion. It does not rust by exposure to air and moisture. When fused in open vessels it absorbs oxygen in considerable quantity, amounting sometimes to 22 times its volume; but it parts with the whole of it in the act of becoming solid. This fact, first noticed by M. Lucas, has been studied by Gay-Lussac, who attributes to it the peculiarly beautiful aspect of granulated silver: he observed the absorption and subsequent evolution of oxygen to be most abundant in the purest silver, and is entirely prevented by a very small per centage of copper. If silver is heated to redness, without fusing, in contact with glass or porcelain, it readily absorbs oxygen, and the oxide fuses with the earthy matters, forming a yellow enamel. When silver in the form of leaves or fine wire is intensely heated by means of electricity, galvanism, or the oxy-hydrogen blow-pipe, it burns with vivid scintillations of a greenish-white colour.

The only pure acids that act on silver are the sulphuric and nitric acids, by both of which it is oxidized, forming with the first a sulphate, and with the second a nitrate of oxide of silver. It is not attacked by sulphuric acid unless by the aid of heat. Nitric acid is its proper solvent, and forms with its oxide a salt, which, after fusion, is known by the name of *lunar caustic.*

From recent experiments on the composition of the chloride and nitrate of the oxide of silver, I have deduced 108 as the eq. of silver, an estimate closely corresponding with the previous researches of Berzelius. (Phil. Trans. 1833, part ii.) Its symb. is Ag. The compounds of silver described in this section are thus constituted :—

	Silver.			Equiv.	Formulæ.
Oxide . .	108 1 eq.	+Oxygen	8	1 eq.=116	Ag+O or AgO.
Chloride .	108 1 eq.	+Chlorine	35·42	1 eq.=143·42	Ag+Cl or AgCl.
Iodide . .	108 1 eq.	+Iodine	126·3	1 eq.=234·3	Ag+I or AgI.
Sulphuret .	108 1 eq.	+Sulphur	16·1	1 eq.=124·1	Ag+S or AgS.

Oxide of Silver.—This oxide may be procured by mixing a solution of pure baryta with nitrate of oxide of silver dissolved in water. It is of a brown colour, insoluble in water, and is completely reduced by a red heat. Gregory has given the following process. The freshly precipitated and well-washed chloride of silver is boiled with aqua potassæ of sp. gr. 1·25 or 1·3, when it is soon converted into a black powder, which is oxide of silver. If a portion of the powder, after being well washed, does not dissolve without residue in diluted nitric acid, the boiling with potash is to be repeated till the powder becomes entirely soluble in nitric acid. The process is facilitated by triturating the moist powder after the first boiling, but the chloride, before it has been acted on by potash, cannot, on account of its flexibility and toughness, be reduced to a fine powder. The oxide of silver, thus prepared, is a very heavy powder of a bluish black, the composition of which is the same as that of the brown precipitated oxide. Oxide of silver combines with acids, forming salts, most of which are insoluble or sparingly soluble. It is separated from the solution of the nitrate by pure alkalies and alkaline earths as the brown oxide, which is redissolved by ammonia in excess; by alkaline carbonates as a white carbonate, which is soluble in an excess of carbonate of ammonia; as a dark-brown sulphuret by hydrosulphuric acid; and as a white curdy chloride of silver, which is turned violet by light, and is very soluble in ammonia, by hydrochloric acid or any soluble chloride. By the last character, silver may be both distinguished and separated from other metallic bodies.

Silver is precipitated in the metallic state by most other metals. When mercury is employed for this purpose, the silver assumes a beautiful arborescent appearance, called *arbor Dianæ*. A very good proportion for the experiment is 20 grains of lunar caustic to 6 drachms or an ounce of water. The silver thus deposited always contains mercury.

When oxide of silver, recently precipitated by baryta or lime-water, and separated from adhering moisture by bibulous paper, is left in contact for 10 or 12 hours with a strong solution of ammonia, the greater part of it is dissolved; but a black powder remains which detonates violently from heat or percussion. This substance, which was discovered by Berthollet, (An. de Chimie, i.) appears to be a compound of ammonia and oxide of silver; for the products of its detonation are metallic silver, water, and nitrogen gas. It should be made in very small quantity at a time, and dried spontaneously in the air. As we we have seen that the nitruret of mercury, formed by the action of ammonia on the oxide is very explosive, it is possible that the fulminating silver may be a nitruret of the metal, with combined or mechanically adhering water.

On exposing a solution of oxide of silver in ammonia to the air, its surface becomes covered with a pellicle, which Faraday considers to be an oxide containing a smaller proportion of oxygen than that just described. This opinion he has made highly probable; but further experiments are requisite before the existence of this oxide can be regarded as certain. Its eq. is 116; symb. $\mathrm{Ag} + \mathrm{O}$, $\dot{\mathrm{Ag}}$, or AgO.

Chloride of Silver.—Prep.—This compound, which sometimes occurs in silver mines, and constitutes the horn silver of mineralogists, is always generated when silver is heated in chlorine gas, and may be prepared conveniently by mixing hydrochloric acid, or any soluble chloride, with a solution of nitrate of oxide of silver. As formed by precipitation it is quite white; but by exposure to the direct solar rays it becomes violet, and almost black, in the course of a few minutes; and a similar effect is slowly produced by diffused daylight. On this principle is founded Mr. Talbot's method of photography. Hydrochloric acid is set free during this change, and, according to Berthollet, the dark colour is owing to separation of oxide of silver. (Statique Chimique, vol. i. p. 195.)

Prop.—It is insoluble in water, and is dissolved very sparingly by the strongest acids; but it is soluble in ammonia. Hyposulphurous acid and its salts likewise dissolve it. At a temperature of about 500° it fuses, and forms a semitransparent horny mass on cooling, which has a density of 5·524. It bears any degree of heat, or even the combined action of pure charcoal and heat, without decomposition; but hydrogen gas decomposes it readily with formation of hydrochloric acid. When boiled with strong aqua potassæ, it is decomposed, chloride of potassium and oxide of silver being formed; and in the dry way it is reduced by fusion with alkalies. Its eq. is 143·42; symb. $\mathrm{Ag} + \mathrm{Cl}$, or AgCl.

Iodide of Silver.—This compound is formed when iodide of potassium is mixed with a solution of nitrate of oxide of silver. It is of a greenish-yellow colour, and is insoluble in water and ammonia. A film of this compound on the surface of a polished plate of silver, constitutes the substance which receives the impressions of light in Daguerre's beautiful invention of the Daguerréotype.

Its eq. is 234·3; symb. $\mathrm{Ag} + \mathrm{I}$, or AgI.

Sulphuret of Silver.—Silver has a strong affinity for sulphur. This metal tarnishes rapidly when exposed to an atmosphere containing hydrosulphuric acid gas, owing to the formation of a sulphuret. On transmitting a current of this gas through a solution of lunar caustic, a dark brown precipitate subsides, which is a sulphuret of silver. The *silver glance* of mineralogists is a similar compound, and the same sulphuret may be prepared by heating thin plates of silver with alternate layers of sulphur. This sulphuret is remarkable for being soft and even malleable. Its eq. is 124·1; symb. $\mathrm{Ag} + \mathrm{S}$, or AgS.

Silver unites also by the aid of heat with phosphorus, forming a soft, brittle, crystalline compound.

SECTION XXV.

GOLD.

Hist. and Prep.—Gold appears to have been known to the earliest races of man, and to have been esteemed by them as much as by the moderns. It has hitherto been found only in the metallic state, either pure or in combination with other metals. It occurs massive, capillary, in grains, and crystallizes in octohedrons and cubes, or their allied forms. It is sometimes found in primary mountains; but more frequently in alluvial depositions, especially among sand in the beds of rivers, having been washed by water out of disintegrated rocks in which it originally existed. There are few countries in which gold washings have not formerly existed; but the principal supply of gold, until lately, has been from South America, and from the gold mines of Hungary. Of late years, rich mines have been opened in the Uralian mountains of Siberia, especially on the Asiatic side of the chain, where separate masses in sand have been found weighing 18 or 20 pounds. Within the last two years, 1845-46, the supply from this quarter has increased so much, that the value of gold is likely to be seriously affected. Rich deposits of gold appear also to exist in some of the southern provinces of North America; and while this work is passing through the press, the discovery of singularly productive veins of gold in Australia has been announced. Gold is generally separated from accompanying impurities by the process of amalgamation, similar to that described in the last section; by which means it is freed from iron and all associated metals, excepting silver. In Hungary the gold is purified by cupellation. The silver, which in variable quantity is present in native gold, may be brought into view by dissolving the gold in nitro-hydrochloric acid. The best mode of separation is that of quartation, which consists in fusing the gold with so much silver that the former may constitute one-fourth of the mass: nitric acid will then dissolve all the silver, and leave the gold. The silver may also be removed by digestion in sulphuric acid.

Prop.—Gold is the only metal which has a yellow colour, a character by which it is distinguished from all other simple metallic bodies. It is capable of receiving a high lustre by polishing, but is inferior in brilliancy to steel, silver, and mercury. In ductility and malleability it exceeds all other metals; but it is surpassed by several in tenacity. Its density is 19·3; when pure it is exceedingly soft and flexible; and it fuses according to Daniell at 2016°.

Gold may be exposed for ages to air and moisture without change, nor is it oxidized by being kept in a state of fusion in open vessels. When intensely ignited by means of electricity or the oxy-hydrogen blowpipe, it burns with a greenish-blue flame, and is dissipated in the form of a purple powder, which is supposed to be an oxide.

Gold is not oxidized or dissolved by any of the pure acids; for it may be boiled even in nitric acid without undergoing any change. Its best solvents are chlorine and nitro-hydrochloric acid; and it appears from the observations of Davy that chlorine is the agent in both cases, since nitro-hydrochloric acid does not dissolve gold, except when it gives rise to the formation of chlorine. It is to be inferred, therefore, that the chlorine unites directly with the gold, and, in fact, gold is dissolved by an aqueous solution of chlorine. But it is supposed by some chemists that the solvent of gold in nitro-hydrocloric acid, is a peculiar acid, the nitro-chlorous, or cholornitrous acid. It is also readily attached by fluorine.

The most convenient method of dissolving it is to digest fragments of the metal in a mixture composed of two measures of hydrochloric and one of nitric acid, until the acid is saturated. The excess of acid is then expelled by evaporating the orange-coloured solution until a a ruby-red liquid remains, which is the neutral terchloride of gold. On adding water, the chloride is dissolved, forming a solution of a gold-yellow colour.

The eq. of gold, estimated from the analysis of the terchloride by Berzelius, is 199·2; its symb. is Au. The composition of its compounds described in this section is as follows:—

	. eq. of Gold.				Equiv.	Formulæ.
Protoxide	199·2	+	Oxygen	8	1 eq. = 207·2	$Au+O$ or AuO.
Binoxide	199·2	+	do.	16	2 eq. = 115·2	$Au+2O$ or AuO_2.
Peroxide	199·2	+	do.	24	3 eq. = 123·2	$Au+3O$ or AuO_3.
Protochloride	199·2	+	Chlorine	35·42	1 eq. = 234·62	$Au+Cl$ or $AuCl$.
Terchloride .	199·2	+	do.	106·26	3 eq. = 305·46	$Au+3Cl$ or $AuCl_3$.
Protiodide .	199·2	+	Iodine	126·3	1 eq. = 325·5	$Au+I$ or AuI.
Teriodide .	199·2	+	do.	378·9	3 eq. = 578·1	$Au+3I$ or AuI_3.
Tersulphuret .	199·2	+	Sulphur	48·3	3 eq. = 247·5	$Au+3S$ or AuS_3.

Protoxide of Gold.—It is obtained by the action of a cold solution of potassa on the protochloride of gold, and is separated as a green precipitate, which is partially soluble in the alkaline solution. It spontaneously changes soon after its preparation into metallic gold and the peroxide.

Its eq. is 207·2; symb. $Au + O$, Au, or AuO.

The *binoxide* is supposed to be the purple oxide which is formed by the combustion of gold; but its composition has not been demonstrated by analysis.

Peroxide.—Prep.—This, the only well-known oxide of gold, is prepared by the action of alkalies on the terchloride, but is obtained quite pure with difficulty. Pelletier recommends that it should be formed by digesting a solution of the terchloride with pure magnesia, washing the precipitate with water, and removing the excess of magnesia by dilute nitric acid. It is apt, however, to retain magnesia, and I am informed by Wagner, of Pesth in Hungary, that the most certain mode of procuring the peroxide is the following. Dissolve one part of gold in the usual way, render it quite neutral by evaporation, and redissolve in 12 parts of water: to the solution add one part of carbonate of potassa dissolved in twice its weight of water, and digest at about 170°. Carbonic acid gradually escapes, and the hydrated peroxide of a brownish-red colour subsides. After being well washed it is dissolved in colourless nitric acid of specific gravity 1·4, and the solution decomposed by admixture with water. The hydrated peroxide is thus obtained quite pure, and is rendered anhydrous by a temperature of 212°.

Prop.—Yellow in the state of hydrate, and nearly black when anhydrous, is insoluble in water, and completely decomposed by solar light or a red heat. Hydrochloric acid dissolves it readily, yielding the common solution of gold; but it forms no definite compound with any acid which contains oxygen. It may indeed be dissolved by nitric and sulphuric acids; but the affinity is so slight that the oxide is precipitated by the addition of water. It combines, on the contrary, with alkaline bases, such as potassa and baryta, apparently forming regular salts, in which it acts the part of a weak acid. This property, which constitutes the difficulty of procuring peroxide of gold quite pure, induced Pelletier to deny that the peroxide of gold is a salifiable base, and to propose for it the name of *auric acid*, its compounds with alkalies being called *aurates*. (An. de Ch. et Ph. xv.) According to Figuier, when the peroxide is boiled with potassa protoxide is deposited, and a true auric acid. AuO_5, remains in combination with the alkali. It has not, however, been obtained in a separate form. 2 eq. of peroxide $2AuO_3 = Au_2O_6$ may yield 1 eq. AuO, and 1 eq. AuO_5.

When recently precipitated peroxide of gold is kept in strong ammonia for about a day, a detonating compound of a deep olive colour is generated, analogous to the fulminating silver described in the last section. According to the analysis of Dumas, its elements are in the ratio of 1 eq. of gold, 2 of nitrogen, 6 of hydrogen, and 3 of oxygen, as expressed by the symbols $Au + N_2 + H_6 + O_3$. With regard to the mode in which these elements are arranged, different opinions may be formed. Dumas thinks the real combination is indicated by the formula $AuN_2 + NH_3 + 3HO$, being a hydrated nituret of gold united with ammonia; but it appears more simple to consider it as a di-aurate of ammonia, expressed by the formula $AuO_3 + 2NH_3$. Its detonation should give rise to metallic gold, water, nitrogen, and ammonia. A similar compound is obtained, and this is the ordinary mode of procuring fulminating gold, by digesting terchloride of gold with an excess of ammonia: a yellow precipitate subsides, the fulminating ingredient of which appears identical with that above described; but a subchloride of gold and ammonia falls at the same time, and adheres so obstinately that it cannot be wholly removed by boiling water. Fulminating gold may be dried at 212°; but friction, or a heat suddenly raised to about 290° or upwards, produces a violent detonation. It is best to make it in small quantities at a time, and to dry it in the open air. (An. de Ch. et Ph. xliv. 167.) The recent discoveries of Schrötter and Plantamour having established the existence of several metallic niturets, and shewn that some of these bodies are highly explosive, it is possible that the true basis of the fulminating gold may be a nituret of the metal.

Its eq. is 123·2; symb. $Au, + 3O$, $\overset{\cdots}{Au}$, or AuO_3.

Chlorides of Gold.—On concentrating the solution of gold to a sufficient extent by evaporation, the terchloride may be obtained in ruby-red prismatic crystals, which are very fusible. It deliquesces on exposure to the air, and is dissolved readily by water without residue. It is also soluble in alcohol and ether; and the latter withdraws it from the aqueous solution. It begins to lose chlorine at a temperature of about 400°, being changed into a brown dry mass, which is a mixture of the protochloride and terchloride, soluble in water. At about 600° the terchloride is completely resolved into the yellow insoluble protochloride, which by boiling in water is changed into metallic gold and the soluble terchloride. At a red heat the protochloride loses its chlorine altogether, and metallic gold remains. Its eq. is 234·62; symb. $Au + Cl$, or $AuCl$.

The terchloride of gold is the usual and most convenient form of obtaining a solution of gold and examining its properties in that state. On adding to the solution sulphate of protoxide of iron, a brown precipitate ensues, which is gold in very fine division, and the solution contains sesquisulphate of peroxide and perchloride of iron. The action is such that

6 eq. Sulphate of Protoxide of Iron	$6\,(FeO, SO_3.)$
and 1 eq. Terchloride of Gold	$Au\,Cl_3.$

yield

2 eq. Sesquisulphate of Peroxide of Iron	$2(Fe_2O_3, 3SO_3.)$
1 eq. Perchloride of Iron, Fe_2Cl_3, and 1 eq. of Gold	$Au.$

The precipitate when duly washed with dilute hydrochloric acid, in order to separate adhering iron, is gold in a state of perfect purity. A similar reduction is effected by most of the metals, and by sulphurous and phosphorous acids, and by oxalic and formic acids with escape of carbonic acid gas. When a piece of charcoal is immersed in a solution of gold, and exposed to the direct solar rays, its surface acquires a coating of metallic gold; and ribands may be gilded by moistening them with a dilute solution of gold, and exposing them to a current of hydrogen or phosphuretted hydrogen gas. When a strong aqueous solution of gold is shaken in a phial with an equal volume of pure ether, two fluids result, the lighter of which is an ethereal solution of gold. From this liquid flakes of metal are deposited on standing, especially by exposure to light, and substances moistened with it receive a coating of metallic gold.* The reduction in most of these instances is owing to the chlorine quitting the gold in obedience to some stronger attraction: metals deprive it directly of its chlorine; and deoxidizing agents do so indirectly by combining with the oxygen of water, while its hydrogen acts on the chlorine.

When protochloride of tin is added to a dilute aqueous solution of gold, a purple-coloured precipitate, called the *purple of Cassius*, is thrown down; and the same substance may be prepared by fusing together 150 parts of silver, 20 of gold, and 35·1 of tin, and acting on the alloy with nitric acid, which dissolves out the silver and leaves a purple residue, containing the tin and gold which were employed. To prevent the oxidation of the tin during fusion, the three metals should be projected into a red-hot black-lead crucible, which contains a little melted borax. When the powder of Cassius is fused with vitreous substances, such as flint-glass, or a mixture of sand and borax, it forms with them a purple enamel, which is employed in giving pink colours to porcelain. The essential cause of the colour is probably a compound of the purple or supposed binoxide of gold with earthy matters, similar to the enamel formed by glass and oxide of silver; the oxide of tin is not essential, since finely divided metallic gold alone will give the same tint of purple. Fuchs has shown that the purple of Cassius is best prepared by means of sesquioxide of tin dissolved in hydrochloric acid.

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* With respect to the revival of gold from its solutions, the reader may consult an Essay on Combustion, by Mrs. Fulhame, and a paper by Count Rumford, in the Philosophical Transactions for 1798.

The chemical nature of the purple of Cassius is very obscure. From its formation by protochloride of tin it is inferred to contain peroxide of tin and gold either in the metallic state or oxidized to a degree inferior to the peroxide. According to Berzelius its sole loss when heated to redness is 7·65 per cent. of water, and the residue has a brick-red colour arising from a mechanical mixture of metallic gold and peroxide of tin, a statement which is confirmed by Gay-Lussac. (An. de Ch. et Ph. xlix. 396.) The proportion of these products corresponds to 5 equivalents of peroxide of tin, 1 of gold, and 6 of water. Nevertheless, the purple of Cassius, as is indicated both by its colour and its solubility in ammonia, is not a mechanical mixture of these ingredients; nor can it well be regarded as a chemical compound of gold and peroxide of tin, since no definite compound of the kind is known to chemists. The more probable supposition is, that it is a hydrated double salt, composed of peroxide of tin as the acid, united with protoxide of tin and binoxide of gold as bases, in such proportion that the oxygen of the gold exactly suffices to convert the protoxide into peroxide of tin. A compound of this nature is expressed by the formula $2(SnO,SnO_2) + (AuO_2,SnO_2) + 6HO$.

The eq. of the terchloride is 305·46; symb. $Au + 3Cl$, or $AuCl_3$.

Sulphuret of Gold.—On transmitting a current of hydrosulphuric acid gas through a solution of gold, a black precipitate is formed, which is a sulphuret. It is resolved by a red heat into gold and sulphur.

Its eq. is 247·5; symb. $Au + 3S$, or AuS_3.

Iodides of Gold.—These compounds have recently been studied by Johnston. (Phil. Mag. and An. ix. 266.) The protiodide falls as a greenish yellow powder, when iodide of potassium is added in excess to a solution of the terchloride of gold. Though insoluble in water, it dissolves in a dilute hot solution of iodide of potassium, from which it crystallizes on cooling in golden yellow scales with triangular and square faces. These crystals generally contain about 12 per cent. of metallic gold mechanically mixed with them. They gradually lose iodine at common temperatures, freely at 150°, and are almost wholly decomposed at 230°.

Its eq. is 325·5; symb. $Au + I$, or AuI.

The teriodide is formed when terchloride of gold is added to a solution of iodide of potassium. It falls as a dark green precipitate, which is insoluble in water, but is soluble in hydriodic acid and in solutions of the iodides of potassium and sodium. It is very prone to decomposition from the easy loss of iodine. It is a haloid acid, and forms crystallizable compounds with haloid bases. Thus, on setting aside the solution formed by digesting it in iodide of potassium, the auro-iodide of potassium is deposited in dark-brownish-red, nearly black needles. These crystals are anhydrous, are more stable than the teriodide, and may be dried at 100° without decomposition. The corresponding salt of sodium is deliquescent. Its eq. is 578·1; symb. $Au + 3I$, or AuI_3.

The compounds of gold with the other non-metallic bodies have been little examined.

SECTION XXVI.

PLATINUM.

Hist.—This valuable metal occurs only in the metallic state, associated or combined with various other metals, such as copper, iron, lead, titanium, chromium, gold, silver, palladium, rhodium, osmium, ruthenium, and iridium. It has hitherto been found chiefly in Brazil, Peru, and other parts of South America, in the form of rounded or flattened grains of a metallic lustre and white colour, mixed with sand and other alluvial depositions. The particles rarely occur so large as a pea; but they are sometimes larger, and a specimen brought from South America by Humboldt was rather larger than a pigeon's egg, and weighed 1088·6 grains. In the year 1826, however, Boussingault discovered it in a syenitic rock in the province of Antioquia in South America, where it occurs in veins associated with gold. Rich mines of gold and platinum have also been discovered in the Uralian Mountains. (Edinburgh Journal of Science, v. 323.)

Prep.—The ore of platinum, purified from iron, copper, lead, silver, &c., by alternate digestion in pure nitric and hydrochloric acids, is dissolved in nitro-hydrochloric acid, and to the diluted solution sal ammoniac, dissolved in water, is added. This causes a copious yellow precipitate of the double chloride of platinum and ammonium, while the rhodium, the palladium, and most of the iridium remain in the mother liquid. The precipitate, after being well washed with cold water, and dried, is ignited in a platinum or porcelain crucible as long as any fumes are given off. The residue is spongy platinum, which is quite pure if the salt had a pure yellow colour; but contains a trace of iridium when the salt has been of an orange-red tint. It is obtained in a dense metallic mass by gradually-applied pressure, followed by gentle hammering at a red heat, and finally at a white heat.

Prop.—Pure platinum has a white colour very much like silver, but of inferior lustre. It is, with the exception of iridium, the heaviest of known metals, its density after forging being about 21·25, and 21·5 in the state of wire. Its malleability is considerable, though far less than that of gold and silver. It may be drawn into wires, the diameter of which does not exceed the 2000th part of an inch. It is a soft metal, and like iron admits of being welded at a high temperature. Wollaston* observed that it is a less perfect conductor of heat than several other metals.

Platinum undergoes no change from the combined agency of air and moisture; and it may be exposed to the strongest heat of a smith's forge without suffering either oxidation or fusion. On heating a small wire of it by means of galvanism or the oxy-hydrogen blow-pipe, it is fused, and afterwards burns with the emission of sparks. Smithson Tennant showed that it is oxidized when ignited with nitre (Phil. Trans. 1797); and a similar effect is occasioned by pure potassa and lithia. It is not attacked by any of the pure acids. Its solvents are chlorine or solutions, such as nitro-hydrochloric acid, which supply chlorine; and it is dissolved with greater difficulty than gold.

The remarkable property observed by Döbereiner in spongy platinum of causing the union of oxygen and hydrogen gases, was formerly mentioned; a property which Dulong and Thenard showed to be also possessed, though in a lower degree, by platinum in its compact form of wire or foil, and by several other metals. (An de Ch. et Ph. xxiii. and xxiv.) Faraday (Phil. Trans. 1834, part i.) has lately discussed, with his wonted ability and success, both the conditions required for the effective action of platinum, and the cause of the phenomenon. The sole conditions are purity of the gases and perfect cleanliness of the platinum. By cleanliness is meant perfect absence of foreign matter, pure water excepted; and this condition is easily secured by fusing pure potassa on its surface, washing off the alkali by pure water, then dipping the platinum in hot oil of vitriol, and again washing with water. In this state platinum foil acts so rapidly at common temperatures on oxygen and hydrogen gases mixed in the ratio of 1 to 2, that it often becomes red hot and kindles the mixture. Handling the platinum, wiping it with a towel, or exposing it to the atmosphere for a few days, suffices to soil the surface of the metal, and thereby diminish or prevent its action. These phenomena are supposed to result from the concurring influence of two forces, the self-repulsive energy of similar gaseous particles, and the adhesive attraction exerted between them and the platinum. Each gas repulsive to itself and not repelled by the platinum, comes into the most intimate contact with that metal, and both gases are so condensed upon its surface that they are brought within the sphere of their mutual attraction and combine. Faraday has given several instances, similar to those which I had occasion to describe some years ago (Jameson's Journal, xi. 99 and 311), where the action of platinum is retarded or altogether prevented by small quantities of certain gases, such as hydrosulphuric acid, carbonic oxide, and olefiant gases. One would be tempted to suppose that these gases act by soiling the metallic surface, though in some respects this explanation is not satisfactory.

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* The reader will find, in the Philosophical Transactions for 1829, some important directions by Dr. Wollaston, both as to the mode of extracting platinum from its ores, and of communicating to the pure metal its highest degree of malleability. The essay receives additional interest from being one of those which were composed during the last illness of this truly illustrious philosopher.

When solutions of platinum are heated with various deoxidizing agents, such as formic acids, formiates, alcohol with alkalies, &c., or when an alloy of zinc and platinum is acted on by nitric acid, platinum is obtained as a finely divided black powder, which absorbs oxygen without chemically combining with it, and transfers it to combustible substances, thus indirectly acting as a powerful oxidizing agent. In this way alcohol and pyroxylic spirit may be converted into acetic and formic acids, sulphurous acid into sulphuric acid, &c. (Döbereiner.) The following is perhaps the best method of preparing platinum in the finely divided state, or platinum black as it is called. The double chloride of platinum and ammonium, in fine powder, is covered with diluted sulphuric acid, and a slip of zinc introduced. Hydrogen gas is disengaged, and the yellow salt is, after some time, entirely changed into a heavy black powder possessed in a very high degree of the very remarkable properties of platinum black.

The eq. of platinum, deduced by Berzelius from the analysis of the bichloride, is 98·8; its symb. is Pt. The composition of its compounds described in this section is as follows:—

	Platinum.			Equiv.	Formulæ.
Protoxide	98·8	1 eq.+Oxygen	8	1 eq.=106·8	$Pt+O$ or PtO.
Binoxide	98·8	1 eq.+ . .	16	2 eq.=114·8	$Pt+2O$ or PtO_2.
Sesquioxide ?	197·6	2 eq.+ . .	24	3 eq.=221·6	$2Pt+3O$ or Pt_2O_3.
Protochloride	98·8	1 eq.+Chlorine	35·42	1 eq.=134·22	$Pt+Cl$ or $PtCl$.
Bichloride	98·8	1 eq.+ . .	70·84	2 eq.=169·64	$Pt+2Cl$ or $PtCl_2$.
Protiodide	98·8	1 eq.+Iodine	126·3	1 eq.=225·1	$Pt+I$ or PtI.
Biniodide	98·8	1 eq.+ . .	252·6	2 eq.=351·4	$Pt+2I$ or PtI_2.
Protosulphuret	98·8	1 eq.+Sulphur	16·1	1 eq.=114·9	$Pt+S$ or PtS.
Bisulphuret	98·8	1 eq.+ . .	32·2	2 eq.=131·0	$Pt+2S$ or PtS_2.

Protoxide of Platinum.—This oxide is prepared by digesting protochloride of platinum in a solution of pure potassa, avoiding a large excess of the alkali, since it dissolves a portion of the oxide and thereby acquires a green colour. In this state it is a hydrate which loses first its water and then oxygen when heated, and dissolves slowly in acids, yielding solutions of a brownish-green tint.

Its eq. is 106·8; symb. $Pt + Cl$, Pt, or PlO.

Binoxide.—This oxide is prepared with difficulty, owing to its disposition, like peroxide of gold, to act rather as an acid than an alkaline base, and either to fall in combination with any alkali by which it is precipitated, or to remain with it altogether in solution. Berzelius recommends that it should be prepared by exactly decomposing sulphate of binoxide of platinum with nitrate of baryta, and adding pure soda to the filtered solution, so as to precipitate about half of the oxide; since otherwise, a sub-salt would subside. The oxide falls in the form of a bulky hydrate, of a yellowish-brown colour, it resembles rust of iron when dry, and is nearly black when rendered anhydrous.

Its eq. is 114·8: symb. $Pt + 2O$, $\ddot{Pt}$, or PtO_2.

Sesquioxide.—This oxide, of a grey colour, is prepared, according to its discoverer Mr. E. Davy, by heating fulminating platinum with nitrous acid; but the nature of the compound so formed has not yet been decisively determined. (Phil. Trans. 1820.)

Protochloride.—When the bichloride is heated to 450°, half of its chlorine is expelled, and the protochloride of a greenish-grey colour remains. It is insoluble in water, sulphuric acid, and nitric acid; but hydrochloric acid partially dissolves it, yielding a red solution. It is also dissolved by long boiling with ammonia, and gives rise in this manner to a remarkable series of compounds which will be described under the head of organic bases containing platinum. At a red heat its chlorine is driven off, and metallic platinum is left. It is dissolved by a solution of the bichloride.

Its eq. is 134·22; symb. $Pt + Cl$, or $PtCl$.

Bichloride of Platinum.—This chloride is obtained by evaporating the solution of platinum in nitro-hydrochloric acid to dryness at a very gentle heat, when it remains as a red hydrate, which becomes brown when its water is expelled. It is deliquescent, and very soluble in water, alcohol, and ether; its solution, if free from the chlorides of palladium and iridum, being of a pure orange-yellow colour. Its ethereal solution is decomposed by light, metallic platinum being deposited.

A solution of platinum is recognized by the following characters. When to an alcoholic or concentrated aqueous solution of the bichloride a solution of chloride of potassium is added, a crystalline double chloride of a pale yellow colour subsides, which is insoluble in alcohol, and sparingly soluble in water: at a red heat it yields chlorine gas, and the residue consists of metallic platinum and chloride of potassium. With a solution of hydrochlorate of ammonia a similar yellow salt falls, which when ignited leaves pure platinum in the form of a delicate spongy mass, the power of which in kindling an explosive mixture of oxygen and hydrogen gases has already been mentioned.

Its eq. is 169·64; symb. Pt + 2Cl, or $PtCl_2$.

Protoiodide of Platinum.—Lassaigne prepared this compound by digesting the protochloride of platinum in a rather strong solution of iodide of potassium, when the protoiodide gradually appeared in the form of a black powder, which is insoluble in water and alcohol. It is not changed by the sulphuric, nitric, and hydrochloric acids, decomposed by the alkalies, and at a red heat gives off its iodine.

Its eq. is 225·1; symb. Pt + I, or PtI.

Periodide of Platinum.—Lassaigne prepares this compound by the action of iodide of potassium on a rather dilute solution of bichloride of platinum. At first the liquid acquires an orange-red and then a claret colour, without any precipitation; but when the solution is boiled a black precipitate subsides, which should be washed with hot water and dried at a heat not exceeding 212°. This biniodide is a black powder, sometimes crystalline, is tasteless and inodorous, insoluble in water, and may be boiled in water without change. By alcohol it is sparingly dissolved, especially when heated. Acids act feebly upon it; but it is decomposed by alkalies, and begins to lose iodine at 270°. (An. de Ch. et Ph. li. 113.)

Its eq. is 351·4; symb. Pt + 2I, or PtI_2.

Protosulphuret of Platinum.—It is formed by heating in a retort the yellow ammoniacal chloride of platinum with half its weight of sulphur until all the sal-ammoniac and excess of sulphur is expelled. The protosulphuret is then left as a grey powder of a metallic lustre. It may also be formed by the action of hydrosulphuric acid on protochloride of platinum. Its eq. is 114·9; symb. Pt + S, or PtS.

Bisulphuret.—It is formed as a brown precipitate, which becomes black when dried, by letting fall a solution of bichloride of platinum drop by drop into a solution of sulphuret of potassium, or by transmitting hydrosulphuric acid gas into a solution of the double chloride of platinum and sodium. (Berzelius.) It should be dried in vacuo by aid of sulphuric acid, since by exposure to the air in a moist state sulphuric acid is generated.

Its eq. is 130; symb. Pt + 2S, or PtS_2.

Fulminating platinum may be prepared by the action of ammonia in slight excess on a solution of sulphate of oxide of platinum. (E. Davy.) It is analogous to the detonating compounds which ammonia forms with the oxides of gold and silver, and may possibly be essentially a nituret of the metal.

SECTION XXVII.

PALLADIUM.—RHODIUM.—OSMIUM.—IRIDIUM.—RUTHENIUM.

The five metals to be described in this section are all contained in the ore of platinum, and have hitherto been procured in very small quantity. When the ore is digested in nitro-hydrochloric acid, the platinum, together with palladium, rhodium, iron, copper, and lead, is dissolved; while a black powder is left consisting of ruthenium, osmium, and iridium, mixed in general with a considerable quantity of titanate of iron, and siliceous minerals.

PALLADIUM.

Hist. and Prep.—Discovered in 1803 by Wollaston (Phil. Trans., 1804 and 1805). On adding bicyanide of mercury dissolved in water to a neutral solution of the ore of platinum, either before or after the separation of that metal by hydrochlorate of ammonia, a yellowish-white flocculent precipitate is gradually deposited, which is cyanuret of palladium. When this compound is heated to redness, the cyanogen is expelled, and pure palladium remains. In order to obtain it in a malleable state, the metal should be heated with sulphur, and the resulting sulphuret purified by cupellation in an open crucible with borax and a little nitre. It is then roasted at a low red heat on a flat brick, and when reduced to a pasty consistence, it is pressed into a square or oblong perfectly flat cake. It is again to be roasted very patiently, at a low red heat, until it becomes spongy on the surface; and when quite cold, it is condensed by frequent tappings with a light hammer. By alternate roastings and tappings the sulphur is burned off, and the metal rendered sufficiently dense to be laminated. Thus prepared it is rather brittle while hot, which Wollaston supposed to arise from a small remnant of sulphur. (Phil. Trans., 1829, p. 7.) Within these few years an ore has been imported from Brazil, which consists entirely of gold and palladium, with a little silver. From this ore it is obtained by melting the alloy with a large proportion of silver, and boiling the new compound with nitric acid, which dissolves every thing but the gold. The silver is precipitated by sea-salt, and the palladium is thrown down from the mother liquid by zinc. It is then dissolved in nitric acid, the solution supersaturated with ammonia, and the ammonia neutralized by hydrochloric acid, when the double chloride of palladium and ammonium is thrown down as a yellow powder, which is treated in the same way as the corresponding salt of platinum.

Prop.—It resembles platinum in colour and lustre. It is ductile as well as malleable, and is considerably harder than platinum. It is used by the dentists as an excellent substitute for gold in fastening artificial teeth. Its sp. gr. varies from 11·3 to 11·8. In fusibility it is intermediate between gold and platinum, and is dissipated in sparks when intensely heated by the oxy-hydrogen blowpipe. At a red heat in oxygen gas its surface acquires a fine blue colour, owing to superficial oxidation; but the increase of weight is so slight as not to be appreciated. It is oxidized and dissolved by nitric acid, and even the sulphuric and hydrochloric acids act upon it by the aid of heat; but its proper solvent is nitro-hydrochloric acid. Its oxide forms beautiful red-coloured salts, from which metallic palladium is precipitated by sulphate of protoxide of iron, and by all the metals described in the foregoing sections, excepting silver, gold, and platinum.

From the analysis by Berzelius of the double chloride of palladium and potassium, the eq. of palladium is inferred to be 53·3. Its symb. is Pd. The composition of its compounds described in this section is as follows:—

	Palladium.				Equiv.	Formulæ.
Protoxide .	53·3	1 eq.+Oxygen	8	1 eq.=	61·3	$Pd+O$ or PdO.
Binoxide .	53·3	1 eq.+ do.	16	2 eq.=	69·3	$Pd+2O$ or PdO_2.
Protochloride .	53·3	1 eq.+Chlorine	35·42	1 eq.=	88·72	$Pd+Cl$ or $PdCl$.
Bichloride .	53·3	1 eq.+ do.	70·84	2 eq.=	124·14	$Pd+2Cl$ or $PdCl_2$.
Protosulphuret	53·3	1 eq.+Sulphur	16·1	1 eq.=	69·4	$Pd+S$ or PdS.

Protoxide of Palladium.—This oxide is obtained as a hydrate of a deep brown colour by decomposing its salts with an excess of carbonate of potassa or soda; and, by washing and heating to low redness, the anhydrous protoxide of a black colour is left. It is also obtained by heating the nitrate at a low red heat. In the anhydrous state it is dissolved with difficulty by acids. When strongly heated it parts with its oxygen. Berzelius says it falls from its salts on the addition of the alkalies as a sub-salt, which is dissolved by the alkali in excess.

Its eq. is 61·3; symb. $Pd + O$, $\dot{Pd}$, or PdO.

Binoxide.—To prepare this oxide Berzelius recommends that a solution of potassa or its carbonate in excess should be poured by little and little on the *solid* bichloride of palladium and potassium, and the materials be well intermixed: water is not first added, because it decomposes the double chloride; and the alkali is not added all at once, because the binoxide would then be dissolved at first, and afterwards separate out as a gelatinous hydrate, which could not be purified by washing. When prepared with the foregoing directions, the binoxide is obtained as a hydrate of a deep yellowish-brown colour, which retains a little potassa in combination; but on heating the solution to 212°, the alkali is dissolved, and the anhydrous black oxide left.

Its eq. is 69·3; symb. $Pd + 2O$, $\ddot{Pd}$, or PdO_2.

Protochloride of Palladium.—It is obtained by evaporating to dryness a solution of palladium in nitro-hydrochloric acid, being left as a brown crystalline hydrate, which becomes black when its water is expelled. It loses its chlorine when strongly heated, and is soluble in water.

Its eq. is 88·72; symb. $Pd + Cl$, or $PdCl$.

The *bichloride* is formed by digesting the protochloride in nitro-hydrochloric acid, and exists only in solution, the colour of which is of so deep a brown as to appear nearly black. It is readily distinguished from the protochloride by yielding with chloride of potassium a double chloride of a red colour; whereas that formed with the protochloride is yellow.

Its eq. is 124·14; symb. $Pd + 2Cl$, or $PdCl_2$.

Protosulphuret of Palladium.—It is readily formed by heating the metal with sulphur, and is a fusible brittle compound of a grey colour.

Its eq. is 69·4; symb. $Pd + S$, or PdS.

RHODIUM.

Hist. and Prep.—This metal was discovered by Woliaston at the time he was occupied with the discovery of palladium. On immersing a thin plate of clean iron into the solution from which palladium and the greater part of the platinum have been precipitated, the rhodium, together with small quantities of platinum, copper, and lead, is thrown down in the metallic state; and on digesting the precipitate in dilute nitric acid, the two last metals are removed. The rhodium and platinum are then dissolved by means of nitro-hydrochloric acid, and the solution, after being mixed with some chloride of sodium, is evaporated to dryness. Two double chlorides result, that of platinum and sodium, and of rhodium and sodium, the former of which is soluble, and the latter insoluble in alcohol; and they may therefore be separated from each other by this menstruum. The double chloride of rhodium is then dissolved in water, and metallic rhodium precipitated by insertion of a rod of zinc.

Prop.—Thus procured, it is in the form of a black powder, which requires the strongest heat that can be produced in a wind furnace for fusion, and when fused has a white colour and metallic lustre. It is brittle, is extremely hard, and has a sp. gr. of about 11. It attracts oxygen at a red heat, a mixture of peroxide and protoxide being formed. It is not attacked by any of the acids when in its pure state; but if alloyed with other metals, such as copper or lead, it is dissolved by nitro-hydrochloric acid, a circumstance which accounts for its presence in the solution of crude platinum. It is oxidized by being ignited either with nitre or bisulphate of potash. When heated with the latter, sulphurous acid gas is evolved, and a double sulphate of peroxide of rhodium and potash is generated, which dissolves readily in hot water, and yields a yellow solution. The presence of rhodium in platinum, iridium, and osmium may thus be detected, and by repeated fusion a perfect separation be accomplished. (Berzelius.)

Chemists are acquainted with two oxides of rhodium. The protoxide is black, and the peroxide, which is the base of the salts of rhodium, is of a yellow colour. Most of its salts are either red or yellow.

From the composition of the double chloride of rhodium and potassium Berzelius considers 52·2 as the eq. of rhodium; its symb. is R, and its compounds described in this section are thus constituted:—

	Rhodium.			Equiv.	Formulæ.
Protoxide .	52·2	1 eq.+Oxygen	8	1 eq.= 60·2	R+O or RO.
Peroxide .	104·4	2 eq.+do.	24	3 eq.=129·4	2R+3O or R_2O_3
Protochloride .	52·2	1 eq.+Chlorine	35·42	1 eq.= 87·62	R+Cl or RCl.
Perchloride .	104·4	2 eq.+do.	106·26	3 eq.=210·66	2R+3Cl or R_2Cl
Sulphuret .	Probably a Protosulphuret.				

Oxides of Rhodium.—The first grade of oxidation has not yet been insulated. The peroxide is generated when pulverulent rhodium is heated to redness in a silver crucible mixed with hydrate of potassa and a little nitre, when the rhodium is oxidized and acquires a coffee-brown colour. To remove the potassa united with the peroxide, the mass is first washed with water and then digested in hydrochloric acid, when it acquires a greenish-grey colour, and is left as a pure hydrate of the peroxide. In this state it is insoluble in acids. If an excess of carbonate of potassa or soda is added to the double chloride of rhodium and potassium, and the solution is evaporated, a gelatinous hydrate falls; but on attempting to dissolve in acid the potassa combined with the peroxide, the latter is also dissolved.

Its eq. is 128·4; symb. $2R + 3O$, $\overset{\cdots}{\underline{R}}$, or R_2O_3.

Chlorides of Rhodium.—The only chloride which has yet been insulated is the perchloride, which Berzelius obtained by adding to a solution of the double chloride of rhodium and potassium silicohydrofluoric acid as long as the double fluoride of potassium and silicon was generated, after which the filtered liquid was evaporated to dryness, and redissolved in water. This perchloride when dry has a dark brown colour, is uncrystalline, and decomposed by a full red heat into chlorine and metallic rhodium. It deliquesces in the air into a brown liquid, and its aqueous solution has a fine red colour, whence its name of rhodium (from ῥόδον, a rose) is derived. (An. de Ch. et Ph. xl. 51.)

Its eq. is 210·66; symb. $2R+3Cl$, or R_2Cl_3.

Sulphuret of Rhodium.—It may be formed by heating rhodium directly with sulphur, fuses at a white heat without decomposition, and has a bluish-grey colour, with a metallic lustre. Wollaston made use of it for procuring the metal in a coherent state, in the same manner as sulphuret of palladium.

OSMIUM.—IRIDIUM.—RUTHENIUM.

Hist.—These metals were discovered by the late Mr. Tennant in the year 1803 (Phil. Trans., 1804), and the discovery of iridium was made about the same time by Descotils in France. The black powder mentioned at the beginning of this section is a compound of iridium and osmium, an alloy which Wollaston detected in the form of flat white grains among fragments of crude platinum. This alloy, which is quite insoluble in nitro-hydrochloric acid, is the source from which iridium and osmium are extracted. The extreme hardness of this alloy has led to a most useful application in the manufacture of pens.

The pen is made of standard gold, which has exactly the proper elasticity and firmness, and tipped with small fragments of the alloy of iridium and osmium, or of a very similar alloy of iridium and platinum. The pens made on this principle by Messrs. Mordan and Hyde, of London, are as easy and pleasant to write with as quill pens, and may be used for many years without the slightest change, as the hardness of the tips is such that they are not perceptibly worn even by fourteen or fifteen years of constant use.

Osmium and Iridium.—*Prep.*—These metals are obtained from the pulverulent residue of the ores of platinum, after that metal together with palladium and rhodium have been removed by digestion in nitro-hydrochloric acid. Wollaston has recommended the following process (Phil. Trans. 1829, p. 8):—The residue is ground into a fine powder with a third of its weight of nitre, and the mixture heated to redness in a silver crucible until it is reduced to a pasty state, when the characteristic odour of oxide of osmium will be perceptible. Dissolve the soluble parts, which contain oxide of osmium in combination with potassa, in the smallest possible quantity of water, and acidulate the solution, introduced into a retort, with sulphuric acid diluted with its own weight of water. By distilling rapidly into a clean receiver as long as osmic fumes pass over, the acid will be collected on its sides in the form of a white crust; and, there melting, it will run down in drops beneath the watery solution, forming a fluid flattened globule at the bottom. As the receiver cools, the acid becomes solid and crystallizes. Frémy has lately published an elaborate memoir on osmium, in which other processes are given, but I can only here refer to the work. Osmium is precipitated from the solution of its acid by all the metals, excepting gold and silver. A convenient mode of reduction is to agitate it with mercury, adding hydrochloric acid to decompose the protoxide of mercury which is formed, and then expelling the mercury and calomel by heat. The osmium is left as a black porous powder, which acquires metallic lustre by friction.

The insoluble parts contain the iridium as oxide in combination with potassa. On digesting the mass in hydrochloric acid, a blue solution is obtained; but it afterwards becomes of an olive-green hue, and subsequently acquires a deep red tint. This variety of colour, which suggested the name of iridium, (*Iris,* the rainbow,) is owing to the successive production of different compounds; but the recent researches of Claus tend to show that some of these colours depend on the presence of ruthenium. The iridium may be precipitated from the solution by any metal except gold and platinum, or it may be obtained by exposing the chloride to a red heat. Wöhler has proposed a very elegant process by which both metals may be obtained on a large scale. (Pog. An. xxxi. 161.) The great advantage of his method is, that it leaves the titanate of iron and other foreign minerals undecomposed. He mixes the residue with an equal weight of fused sea-salt in fine powder. The mixture is introduced into a long and wide green glass tube, which is connected at one extremity with an apparatus for developing chlorine, at the other with a tubulated receiver. The latter is furnished with a small tube, the extremity of which is made to dip into a weak solution of ammonia. The tube containing the mixture of salt and ore being then brought to a low red heat, the chlorine is developed and the gas transmitted in a moderate stream through the glowing mass, by which in the first part of the process it is abundantly and completely absorbed. The operation is to be continued until the chlorine is observed to pass pretty freely into the solution of ammonia. The changes which occur are owing to the formation of two haloid acids, by the combination of the chlorine with both metals of the ore; and as these instantly combine with the chloride of sodium, two soluble salts, the iridio-chloride of sodium, and the osmio-chloride of sodium, are produced. But by the moisture of the chlorine gas the latter compound is decomposed, the chloride of osmium giving rise to the formation of osmic and hydrochloric acids, and the deposition of a part of the osmium in the metallic state.

This, by again combining with chlorine, gives rise to a repetition of the same changes, and to the production of an additional quantity of osmic acid, which, being volatile, passes on and is deposited in crystals in the receiver. The solution of ammonia prevents the loss of any osmic acid which might escape condensation. The solid matter in the tube is then digested in water, when a deep brown solution is obtained, and the clear liquid is separated by decantation from the insoluble parts, which consists principally of titanate of iron. As the solution still contains some osmic acid, it is submitted to a distillation until one-half has passed over into a weak solution of ammonia. The remainder is then evaporated in an open dish, while carbonate of soda is at the same time added in successive portions until a considerable excess is present. On evaporating to dryness, a black mass is obtained, which is to be exposed to a low red heat in a hessian crucible. When cold, the saline matter is removed by boiling water, and the sesquioxide of iridium is left in the form of a black powder. It is readily reduced to the metallic state by a stream of hydrogen gas.

Osmium.—As obtained by precipitation it is a black porous powder, which acquires metallic lustre by friction. After exposure to a very gentle heat, its sp. gr. is 7. It takes fire when heated in the open air, and is readily oxidized and dissolved by fuming nitric acid; but a red heat gives it greater compactness, and in that state it ceases to be attacked by acids, and may be freely heated without oxidation. In its densest state Berzelius found its sp. gr. to be 10. (An. de Ch. et Ph. xl. 257, and xlii. 185.) Its symb. is Os.

Berzelius, from his late researches on the compounds of osmium, considers 99·7 to be its eq., and gives the composition of its oxides, chlorides, and sulphurets, as follows:—

	Osmium.			Equiv.	Formulæ.
Protoxide .	99·7	1 eq.+Oxygen	8	1 eq.=107·7	$Os+O$ or OsO.
Sesquioxide .	199·4	2 eq.+do.	24	3 eq.=223·4	$2Os+3O$ or Os_2O_3.
Binoxide .	99·7	1 eq.+do.	16	2 eq.=115·7	$Os+2O$ or OsO_2.
Teroxide .	99·7	1 eq.+do.	24	3 eq.=123·7	$Os+3O$ or OsO_3.
Osmic Acid .	99·7	1 eq.+do.	32	4 eq.=131·7	$Os+4O$ or OsO_4.
Protochloride	99·7	1 eq.+Chlorine	35·42	1 eq.=135·12	$Os+Cl$ or $OsCl$.
Sesquichloride	199·4	2 eq.+do.	106·26	3 eq.=205·66	$2Os+3Cl$ or Os_2Cl_3.
Bichloride .	99·7	1 eq.+do.	70·84	2 eq.=170·54	$Os+2Cl$ or $OsCl_2$.
Terchloride .	99·7	1 eq.+do.	106·26	3 eq.=205·96	$Os+3Cl$ or $OsCl_3$.
Protosulphuret	99·7	1 eq.+Sulphur	16·1	1 eq.=115·8	$Os+S$ or OS or OsS.
Sesquisulphuret	199·4	2 eq.+do.	48·3	3 eq.=247·7	$2Os+3S$ or Os_2S_3.
Bisulphuret .	99·7	1 eq.+do.	32·2	2 eq.=131·9	$Os+2S$ or OsS_2.
Tersulphuret	99·7	1 eq.+do.	48·3	3 eq.=148·0.	$Os+3S$ or OsS_3.

Oxides of Osmium.—For a minute description of these compounds I refer to the essays of Berzelius above cited. The protoxide is precipitated by pure alkalies from the protochloride, and falls as a deep green, nearly black, hydrate, which is soluble in acids, and detonates when heated with combustible matter. The binoxide is thrown down as a hydrate of a deep brown colour, when a saturated solution of the bichloride is heated with carbonate of soda. It retains a little alkali in combination ; but the soda is easily removed by dilute hydrochloric acid, without the oxide being dissolved. The teroxide is prepared in like manner from the terchloride. Frémy has shewn that the binoxide has acid properties, and has called it osmious acid. It forms a crystallizable salt with potash. The sesquioxide has not been obtained in a separate state ; but it is procured in combination with ammonia when the binoxide is treated with a large excess of pure ammonia, nitrogen gas being disengaged at the same time.

The highest stage of oxidation is the volatile acid, which is the product of the oxidation of osmium by acids, by combustion, or by fusion with nitre or alkalies ; and it may be procured by the process above mentioned in colourless transparent elongated crystals, or as a colourless solution in water. Its vapour is very acrid, exciting cough, irritating the eyes, and producing a copious flow of tears ; and its odour is disagreeable and pungent, somewhat like that of chlorine ; a property which suggested the name of *Osmium* (from *οσμη*, odour). It does not combine with acids : on the contrary, though it has no acid reaction, it unites with alkalies, and the compound sustains a strong heat without decomposition. When touched, it communicates a stain which cannot be removed by washing. With the infusion of gall-nuts it yields a purple solution, which afterwards acquires a deep blue tint; a character which forms a sure and extremely delicate test for peroxide of osmium. By sulphurous acid it is deoxidized, and the colour of the solution passes through the shades of yellow, orange, brown, green, and lastly blue, when it resembles sulphate of indigo. These changes correspond to sulphates of the different oxides of osmium, the last or blue oxide being a compound of protoxide and sesquioxide of osmium.

Chlorides of Osmium.—Berzelius has described four chlorides of osmium, corresponding to the first four degrees of oxidation above mentioned. When osmium is heated in a tube in a current of dry chlorine gas, a deep green sublimate is formed, which is the protochloride. On continuing the process it yields a red sublimate, which is the bichloride. For the remaining details, which are rather minute, I may refer to the essay already cited. Several of these chlorides yield double compounds with sodium, potassium, and ammonium, analogous to the double chlorides formed by platinum and palladium.

Osmium unites with sulphur in the dry way, or when precipitated from the chlorides by hydrosulphuric acid. The sulphurets obviously correspond to the number of the oxides. (Berzelius.)

Iridium.—Prop.—A brittle metal, and apt to fall into powder when burnished; but with care it may be polished, and then acquires the appearance of platinum. Of all known metals it is the most infusible: Children, by means of his large galvanic battery, fused it into a globule of a brilliant metallic lustre and white colour, having a density of 18·68; but the attempts at fusion by Berzelius were unsuccessful. Breithaupt states that the sp. gr. of native iridium, lately found in the Russian mines of platinum, although not quite free from lighter metals, varies from 23 to 26. This would make iridium the heaviest of metals. It is also, according to Breithaupt, the hardest and the most indestructible by acids. Hence, if it could be easily wrought it would be invaluable for the edges of delicate balances, and it is this extreme hardness, found also in the native alloys of iridium, that renders them so admirably adapted for the tips of metallic pens. It is oxidized at a red heat in the open air, if in a state of fine division, but not otherwise; and it is attacked with difficulty even by nitro-hydrochloric acid.

The eq. of iridium is estimated by Berzelius at 98·8, being identical with that of platinum. It forms with oxygen four oxides exactly analogous in composition to the four first oxides of osmium in the foregoing table, and its four chlorides correspond to those of osmium. Its sulphurets have been little examined, but they doubtless correspond to the oxides. (An. de Ch. et Ph. xl. 257, and xliii. 185.) Its symb. is Ir.

Oxides of Iridium.—The protoxide, sesquioxide, and teroxide are precipitated by alkalies from the chloride, to which each is respectively proportional. The protoxide is greenish-grey as a hydrate, and black when anhydrous. The sesquioxide is bluish-black in the dry state, and deep brown as a hydrate. The hydrated teroxide is of a yellowish-brown or greenish colour. The binoxide has not hitherto been fully studied. Berzelius has not fully decided the nature of the compound which is considered as the blue oxide, that which forms a blue solution with acids; but he believes it to be a compound of the protoxide and sesquioxide. Claus states that it is the binoxide, and that it is very permanent when pure. This variety of oxides, together with the facility with which they appear to pass from one to the other, amply accounts for the diversity of tints sometimes observed in solutions of iridium; but there is reason to believe that some of these colours depend on the presence of ruthenium.

Chlorides of Iridium.—The protochloride is obtained as a light powder of a deep olive-green colour, by transmitting chlorine gas over pulverulent iridium heated to a commencing red heat. When heated to redness its chlorine is expelled. It is insoluble in water, and but sparingly dissolved by acids, even the nitro-hydrochloric; but when the hydrated protoxide is digested in hydrochloric acid, the protochloride is reproduced and dissolved, forming probably a soluble compound of the protochloride and hydrochloric acid. Its solution is a mixture of brown, green, and yellow. (Berzelius.)

Its eq. is 134·25 ; symb. $IrCl$.

The *sesquichloride* is best obtained by calcining iridium with nitre, digesting the product in nitric acid, and, after washing, dissolving the residual oxide in hydrochloric acid. Its solution has a dark yellowish-brown tint, which is so intense that a small quantity renders water opaque. By evaporation it yields a black mass, wholly uncrystalline, and deliquescent in the air. Its eq. is 303·9; symb. Ir_2Cl_3.

The *bichloride* is formed by digesting at a moderate heat the sesquichloride in nitro-hydrochloric acid. It is deliquescent and very soluble, yielding a solution of a dark reddish-brown colour. When its solution is evaporated to dryness, except at a heat not exceeding 104°, it loses chlorine, and is reconverted into the sesquichloride.

The *terchloride* has not been obtained in a separate form, but only as a double chloride of potassium. It appears to be the principal compound formed in the process above given for extracting iridium from its ore, and is recognized by its rose-red tint.

Iridium has a considerable affinity for carbon, combining with it when a piece of metal is held in the flame of a spirit-lamp. The resulting carburet contains 19·8 per cent. of carbon.

Ruthenium.—This metal has been lately discovered by Claus in the insoluble residue of the ore of platinum. Osann, a good many years ago, gave this name to a supposed new metal which he believed to exist in the ore of platinum; and Claus, who has studied it and demonstrated its existence, has retained the name proposed by Osann.

The new metal is separated from the others which accompany it by a process founded on the property possessed by its sesquioxide, as well as that of osmium, of being decomposed by boiling with water, and depositing sesquioxide, for which I must refer to Claus's paper, Annalen der Chemie, lix. 234.

Ruthenium is a metal of a grey colour, very infusible. It has a stronger attraction for oxygen than any of the other metals of this class, for it can be oxidized by igniting it in the air, and the oxide is not reduced by a red heat. The oxide forms a soluble compound with potash. Ruthenium seems to bear the same relation to rhodium that iridium does to platinum, for it has the same atomic weight as rhodium, and forms oxides and chlorides corresponding to those of that metal.

It is distinguished from rhodium and iridium by the brownish-red colour of its salts, by its greater attraction for oxygen, and by the circumstance that the double chloride of ruthenium and potassium or sodium is soluble, under certain circumstances, in alcohol, in which fluid the corresponding salts of rhodium and iridium are insoluble.

Another peculiarity is, that its solutions are not entirely precipitated by hydrosulphuric acid (sulphuretted hydrogen), and that the supernatant liquid has a fine blue colour, not observed with any of the allied metals. The same blue colour is observed when solutions of ruthenium are precipitated by zinc or by bicyanide of mercury. The cause of this appearance is not yet fully ascertained; but Claus ascribes it to the presence of a soluble modification of the protochloride.

Oxides of Ruthenium.—Claus has described four oxides, namely, the protoxide, RuO; the sesquioxide, Ru_2O_3; the binoxide, RuO_2; and the teroxide RuO_3. The last he conjectures to be an acid; but it is very prone to decomposition.

Chlorides of Ruthenium.—Claus has also described three chlorides. The protochloride, $RuCl$, when prepared in the dry way, is black, crystalline, and insoluble. The sesquichloride, Ru_2Cl_3, is soluble and orange-yellow: when acted on by sulphuretted hydrogen, it yields a fine blue solution, which Claus believes to contain a soluble modification of the protochloride. The terchloride is only known in its double compounds with other chlorides, which have a rose red colour. The sesquichloride also forms double chlorides. The sulphurets of ruthenium appear to correspond with the oxides.

The paper of Claus, just published, contains details which render it highly probable that the description above given of iridium does not apply to the pure metal and its compounds, but to a mixture of iridium and ruthenium. The two metals are in many respects analogous; but we must wait for a promised publication by Claus, for a description of the compounds of pure iridium, which, according to him, differ in many points from the account above given on the authority of Berzelius previous to the discovery of ruthenium.

SECTION XXVIII.

ON METALLIC COMBINATIONS.

Having completed the history of the individual metals, and of the compounds resulting from their union with the simple non-metallic bodies, I shall treat briefly in the present section of the combinations of the metals with each other. These compounds are called *alloys;* and to those alloys of which mercury is a constituent, the term *amalgam* is applied. It is probable that each metal is capable of uniting in one or more proportions with every other metal, and on this supposition the number of alloys would be exceedingly numerous. This department of chemistry, however, owing to its having been cultivated with less zeal than most other branches of the science, is as yet limited, and our knowledge concerning it imperfect. On this account I shall mention those alloys only to which some particular interest is attached.

Metals do not combine with each other in their solid state, owing to the influence of chemical affinity being counteracted by the force of cohesion. It is necessary to liquefy at least one of them, in which case they always unite, provided their mutual attraction is energetic. Thus, brass is formed when pieces of copper are put into melted zinc; and gold unites with mercury at common temperatures by mere contact.

Metals appear to unite with one another in every proportion, precisely in the same manner as sulphuric acid and water. Thus there is no limit to the number of alloys of gold and copper. It is certain, however, that metals have a tendency to combine in definite proportion; for several atomic compounds of this kind occur native. The crystallized amalgam of silver, for example, is composed, according to the analysis of Klaproth, of 64 parts of mercury and 36 of silver; numbers which are so nearly in the ratio of 202 to 108, that the amalgam may be inferred to contain one eq. of each of its elements. It is indeed possible that the variety of proportion in alloys is rather apparent than real, arising from the mixture of a few definite compounds with each other, or with uncombined metal; an opinion not only suggested by the mode in which alloys are prepared, but in some measure supported by observation. Thus, on adding successive small quantities of silver to mercury, a great variety of fluid amalgams are apparently produced; but, in reality, the chief, if not the sole compound, is a solid amalgam, which is merely diffused throughout the fluid mass, and may be separated by pressing the liquid mercury through a piece of thick leather.

This view is strengthened by some late experiments by Rudberg. (An. de Ch. et Ph. xlviii. 363.) He finds that variable mixtures of metals in cooling after fusion have generally two periods when the thermometer is stationary. In alloys of lead and tin one of these points is uniformly at 368½° for all mixtures, while the other point varies according as one or the other metal is predominant, and is near the fusing point of the predominating metal. From this it is inferred that the latter point is caused by the congelation of the predominating metal, and the constant point is the congealing temperature of an alloy of uniform composition present in all the mixtures. This alloy is composed of 3 eq. of tin and 1 eq. of lead, its congealing point being 368½°. In variable mixtures of bismuth and tin the constant point is 289½°, which is the congealing temperature of an alloy composed of single eqs. of tin and bismuth.

Alloys are exactly similar to metals in their chief physical properties. They are opaque, possess the metallic lustre, and are good conductors of heat and electricity. They often differ materially in some respects from the elements of which they consist. The colour of an alloy is sometimes different from that of its constituents, of which brass is a remarkable example. The hardness of a metal is in general increased by being alloyed, and for this reason its elasticity and sonorousness are frequently improved. The malleability and ductility of metals, on the contrary, are usually impaired by combination. Alloys formed of two brittle metals are always brittle; and an alloy composed of a ductile and a brittle metal is generally brittle, especially if the latter predominate. An alloy of two ductile metals is sometimes brittle.

The density of an alloy is sometimes less, sometimes greater, than the mean density of the metals of which it is composed.

The fusibility of metals is greatly increased by being alloyed. Thus, pure platinum, which cannot be completely fused in the most intense heat of a wind furnace, forms a very fusible alloy with arsenic, or with zinc.

The tendency of metals to unite with oxygen is considerably augmented by being alloyed. This effect is particularly conspicuous when dense metals are liquefied by combination with quicksilver. Lead and tin, for instance, when united with mercury, are soon oxidized by exposure to the atmosphere; and even gold and silver combine with oxygen, when the amalgams of those metals are agitated with air. The oxidability of one metal in an alloy appears in some instances to be increased in consequence of a galvanic action. Thus, Faraday observed that an alloy of steel with 100th of its weight of platinum was dissolved with effervescence in dilute sulphuric acid, which was so weak that it scarcely acted on common steel; an effect which he ascribes to the steel in the alloy being rendered positive by the presence of the platinum. De la Rive has noticed a similar instance in commercial zinc, the oxidability of which is increased by the presence of small quantities of iron. In these cases, however, the effect is due rather to one metal being mechanically enveloped in another than to actual combination.

AMALGAMS, OR ALLOYS CONTAINING MERCURY.

Quicksilver unites with potassium when agitated in a glass tube with that metal, forming a solid amalgam. When the amalgam is put into water, the potassium is gradually oxidized, hydrogen gas is disengaged, and the mercury resumes its liquid form. A similar compound may be obtained with sodium. These amalgams may also be procured by placing the negative wire in contact with a globule of mercury during the process of decomposing potassa and soda by galvanism.

A solid amalgam of tin is employed in making looking-glasses; and an amalgam made of one part of lead, one of tin, two of bismuth, and four parts of mercury, is used for silvering the inside of hollow glass globes. This amalgam is solid at common temperatures; but it is fused by a slight degree of heat.

The amalgam of zinc and tin, used for promoting the action of the electrical machine, is made by fusing one part of zinc with one of tin, and then agitating the liquid mass with two parts of hot mercury placed in a wooden box. Mercury evinces little disposition to unite with iron, and, on this account, it is usually preserved in iron bottles.

The amalgam of silver, as already mentioned, is a mineral production. The process of separating silver from its ores by amalgamation, practised on a large scale at Freyberg in Germany, is founded on the affinity of mercury for silver. On exposing the amalgam to heat, the quicksilver is volatilized, and pure silver remains.

Gold unites with remarkable facility with mercury, forming a white-coloured compound. An amalgam composed of one part of gold and eight of mercury is employed in gilding brass. The brass after being rubbed with nitrate of oxide of mercury, in order to give it a thin film of quicksilver, is covered with the amalgam of gold, and then exposed to heat for the purpose of expelling the mercury.

ALLOYS OF ARSENIC.

Arsenic has a tendency to render the metals with which it is alloyed both brittle and fusible. It has the property of destroying the colour of gold and copper. An alloy of copper with a tenth part of arsenic, is so very similar in appearance to silver, that it has been substituted for it. The whiteness of this alloy affords a rough mode of testing for arsenic; for if arsenious acid and charcoal be heated between two plates of copper, a white stain afterwards appears upon its surface, owing to the formation of an arseniuret of copper.

The presence of arsenic in iron has a very pernicious effect; for even though in small proportion, it renders the iron brittle, especially when heated.

The alloy of tin and arsenic is employed for forming arseniuretted hydrogen gas by the action of hydrochloric acid. The tin of commerce sometimes contains a minute quantity of this alloy.

An alloy of platinum with ten parts of arsenic is fusible at a heat a little above redness, and may therefore be cast in moulds. On exposing the alloy to a gradually increasing temperature in open vessels, the arsenic is oxidized and expelled, and the platinum recovers its purity and infusibility.

ALLOYS OF TIN, LEAD, ANTIMONY, AND BISMUTH.

Tin and lead unite readily when fused together, constituting solder, of which two kinds are distinguished. The alloy called *fine solder* consists of two parts of tin and one of lead, fuses at about 360°, and is much employed in tinning copper. The *coarse solder* contains 1-4th of tin, fuses at about 500°, and is the substance used for soldering by glaziers. Thus, by varying the relative quantity of the metals, a solder of different fusibility may be obtained. The process of hard soldering or *brazing*, by which two surfaces of copper are cemented together, is done with *hard solder*, which is made by fusing together brass and zinc: the copper requires to be heated, when this solder is used, to near its point of fusion.

It has been observed by Kupfer that most of the *alloys* of tin and lead, made in atomic proportion, have a sp. gr. less than their calculated density; from which it is manifest that they expand in uniting. The *amalgams* of lead and tin, on the contrary, occupy less space, when combined, than their elements did previously.

Tin alloyed with small quantities of antimony, copper, and bismuth, forms the best kind of pewter. Inferior sorts contain a large proportion of lead.

Tin, lead, and bismuth form an alloy which is fused at a temperature below 212°. The best proportion, according to D'Arcet, is 8 parts of bismuth, 5 of lead, and 3 of tin.

An alloy of 3 parts of lead to 1 of antimony constitutes the substance of which types for printing are made.

A native alloy of antimony and nickel, found at Andreasberg in the Harz, was shewn by Stromeyer to consist of 29·5 parts or 1 eq. of nickel, and 64·4 parts or 1 eq. of antimony.

ALLOYS OF COPPER.

Copper forms with tin several valuable alloys, which are characterized by their sonorousness. Bronze is an alloy of copper with about eight or ten per cent. of tin, together with small quantities of other metals which are not essential to the compound. Cannons are cast with an alloy of a similar kind.

The best bell-metal is composed of 80 parts of copper and 20 of tin; the Indian gong, celebrated for the richness of its tones, contains copper and tin in this proportion. A specimen of English bell-metal was found by Dr. Thomson to consist of 80 parts of copper, 10·1 of tin, 5·6 of zinc, and 4·3 of lead. Lead and antimony, though in small quantity, have a remarkable effect in diminishing the elasticity and sonorousness of the compound. *Speculum-metal*, with which mirrors for telescopes are made, consists of about two parts of copper and one of tin. The whiteness of the alloy is improved by the addition of a little arsenic.

Copper and zinc unite in several proportions, forming alloys of great importance in the arts. The best brass consists of four parts of copper to one of zinc; and when the latter is in a greater proportion, compounds are generated which are called *Tombac*, *Dutch-gold*, and *Pinchbeck*. The *white copper* of the Chinese, which is the same as the German silver of the present day, is composed, according to the analysis of Fyfe, of 40·4 parts of copper, 25·4 of zinc, 31·6 of nickel, and 2·6 of iron; but there are are many different varieties of this useful alloy. The best kinds are those which contain the largest proportion of nickel, up to a certain limit. They can hardly be distinguished from silver plate.

The art of tinning copper consists in covering that metal with a thin layer of tin, in order to protect its surface from rusting. For this purpose, pieces of tin are placed upon a well-polished sheet of copper, which is heated sufficiently for fusing the tin. As soon as the tin liquefies, it is rubbed over the whole sheet of copper, and if the process is skilfully conducted, adheres uniformly to its surface. The oxidation of the tin, a circumstance which would entirely prevent the success of the operation, is avoided by employing fragments of resin or muriate of ammonia, and regulating the temperature with great care. The two metals do not actually combine; but the adhesion is certainly owing to their mutual affinity.—Iron, which has a weaker attraction than copper for tin, is tinned with more difficulty than that metal.

ALLOYS OF IRON.

The alloys of iron have been little studied; but Mr. Morries Stirling has just taken out a patent for several alloys of iron with different metals, which possess most valuable properties. As the specification has not yet been given in, no details can here be given; but there can be no doubt that several of these alloys will prove highly important. Most, if not all of them, are fusible enough to be easily cast, and they much excel cast iron in hardness and toughness. Some of them are remarkably sonorous.

ALLOYS OF STEEL.

Messrs. Stodart and Faraday have succeeded in making some very important alloys of steel with other metals. (Phil. Trans. for 1822.) Their experiments induced them to believe that the celebrated Indian steel, called *wootz,* is an alloy of steel with small quantities of silicon and aluminium; and they succeeded in preparing a similar compound, possessed of all the properties of wootz. They ascertained that silver combines with steel, forming an alloy, which, although it contains only 1-500th of its weight of silver, is superior to wootz or the best cast steel in hardness. The alloy of steel with 100th part of platinum, though less hard than that with silver, possesses a greater degree of toughness, and is therefore highly valuable when tenacity as well as hardness is required. The alloy of steel with rhodium even exceeds the two former in hardness. The compound of steel with palladium, and of steel with iridium and osmium, is likewise exceedingly hard; but these alloys cannot be employed extensively, owing to the rarity of the metals of which they are composed.

ALLOYS OF SILVER.

Silver is capable of uniting with most other metals, and suffers greatly in malleability and ductility by their presence. It may contain a large quantity of copper without losing its white colour. The standard silver for coinage contains about 1-13th part of copper, which increases its hardness, and thus renders it more fit for coins and many other purposes.

ALLOYS OF GOLD.

The presence of other metals in gold has a remarkable effect in impairing its malleability and ductility. The metals which possess this property in the greatest degree are bismuth, lead, antimony, and arsenic. Thus, when gold is alloyed with 1-1920th part of its weight of lead, its malleability is surprisingly diminished. A very small proportion of copper has an influence over the colour of gold, communicating to it a red tint, which becomes deeper as the quantity of copper increases. Pure gold, being too soft for coinage and many purposes in the arts, is always alloyed either with copper or an alloy of copper and silver, which increases the hardness of the gold without materially affecting its colour or tenacity. Gold coins contain about 1-12th of copper.

Nearly all the gold found in nature is alloyed more or less with silver. In a late elaborate investigation into the constituents of the Uralian ores of gold, G. Rose found one specimen with 0·16 per cent. of silver, and another with 38·38 per cent.; but most of the specimens contained 8 or 9 per cent. of silver. It has been maintained that the native alloys of gold and silver are usually in atomic proportion. This statement, however, has been amply disproved by G. Rose; these metals appear to be isomorphous, and hence, like other isomorphous bodies, they crystallize with each other in proportions altogether indefinite. (Pog. An. xxiii. 161.)

SALTS.

GENERAL REMARKS ON SALTS.

The preceding pages contain the description either of elementary principles or of compounds immediately resulting from the union of those elements. These compounds are chiefly bi-elementary, that is, arise from the union of two elements; their constituents are regarded, according to the electro-chemical theory, as possessing opposite electric energies, and as combined by virtue of such energies; and the names applied to them are partly constructed in reference to this theory. Thus in compounds of oxygen and chlorine, chlorine and iodine, sulphur and potassium, the term expressive of the genus or class of bodies to which each compound belongs, is derived from the electro-negative element; so that we do not say, chloride of oxygen, iodide of chlorine, and potassiuret of sulphur,—but, oxide of chlorine, chloride of iodine, and sulphuret of potassium; because oxygen has a higher electro-negative energy than chlorine, chlorine than iodine, and sulphur than potassium. The metals as a class are electro-positive to the non-metallic elements; but in relation to each other some of the metals are electro-positive, and others electro-negative. To the former belong those metals the oxides of which are strong alkaline bases, such as potassium, sodium, and calcium; and among the latter are enumerated those, such as arsenic, antimony, and molybdenum, which are prone to form acids when they unite with oxygen.

Some of the bi-elementary compounds above referred to, though composed of very energetic elements, are themselves chemically indifferent, manifesting little disposition to unite with any other body whatever; of which the peroxides of manganese and lead, and some of the chlorides, are examples. Others, on the contrary, are surprisingly energetic in their chemical relations, and have an extensive range of affinity. The most remarkable instances of this are found among those oxidized bodies called *acids* and *alkalies*, the characters of which fixed the attention of chemists long before their composition was understood. The acids and alkalies, however, are indifferent to elementary substances: their affinities are exerted towards each other, and by uniting they give rise to compounds more complex than themselves, as containing at least three elements, and which are known by the name of *salts*. Acids and alkalies possess opposite electric energies in relation to each other, the former being — and the latter +. The electric energies evinced by them are related to the electric energies of their elements. Thus acids generally abound in the electro-negative oxygen, and if they contain a metal, it is usually an electro-negative metal; whereas the powerful alkalies are the protoxides of electro-positive metals, containing only 1 eq. of oxygen.

Acids and alkalies neutralize each other more or less completely, so that the resulting salt is generally neither acid nor alkaline, and is far less energetic as a chemical agent than acids and alkalies. Most of them, however, unite in definite proportion with certain substances, such as water, alcohol, ammonia, and with other salts, forming the extensive family of *double salts.* To these compounds the electro-chemical theory may be extended: the two simple salts which constitute a double salt, may be viewed as two molecules united by virtue of electric energies of an opposite character.

In the early period of modern chemistry an acid was considered to be an oxidized body which has a sour taste, reddens litmus paper, and neutralizes alkalies. But subsequent experience has shewn the propriety of extending the definition of an acid. For, first, the discovery of the hydracids proved that oxygen is not essential to acidity. Secondly, some compounds, owing to their insolubility, neither taste sour nor redden litmus, and yet from their chemical relations are regarded as acids. Thirdly, some acknowledged acids, such as the carbonic and hydrosulphuric, are unable fully to destroy the alkaline reaction of potassa. Facts of this kind have induced chemists to consider as acids all those compounds which unite with potassa or ammonia, and give rise to bodies similar in their constitution and general character to the salts which the sulphuric or some admitted acid forms with those alkalies.

A similar extension is given to the notion of alkalinity, the characters of which, as exhibited in their most perfect form in potassa and soda, are causticity, a peculiar pungent alkaline taste, alkaline reaction with test paper, and power both of neutralizing acids and of forming with them neutral saline compounds. Of these, chemists agree to consider the last as the most characteristic, and place among the *alkaline or salifiable bases* all those bodies which unite definitively with admitted acids, such as the sulphuric and nitric, and form with them compounds analogous in constitution to the salts which admitted alkalies form with the acids. Thus, magnesia is a very strong alkaline base, seeing that 20·7 parts of it neutralize as much sulphuric acid as 47 of potassa; and yet magnesia, from being insoluble, is all but tasteless, and has barely any alkaline reaction.

The progress of chemistry, which has gradually developed sounder views of the nature of acids and alkalies, is also causing an extension in the idea of a salt. The great mass of the salts are compounds of oxidized bodies, both the acid and the base containing oxygen. But ammonia, though not an oxide, has all the characters of alkalinity in an eminent degree, and its compounds with acids were at once admitted into the list of salts. Then came the discovery of the hydracids, such as the hydrochloric and hydriodic, which are so powerfully acid, that their compounds with alkaline bases were readily adopted as salts. Hence arose the division of the salts as a class into two orders, one containing the oxygen or oxy-salts, and the other the hydrogen or hydro-salts. Again, the gaseous terfluoride of boron, which contains neither oxygen nor hydrogen, combines definitely with ammonia, and forms with it a neutral compound, which was esteemed a salt as soon as it was known.

The notion of a salt has of late been still further extended. Chemists have long known that metallic sulphurets occasionally combine together, and constitute what is called a *double sulphuret.* In these compounds Berzelius, whose labours have greatly added to their number, has traced an exact analogy with the oxygen salts, and applied to them the name of *sulphur-salts.* The simple sulphurets, by the union of which a sulphur-salt is formed, are bi-elementary compounds, strictly analogous in their constitution to acids and alkaline bases, and which, like them, are capable of assuming opposite electric energies in relation to each other. Electro-positive sulphurets, termed *sulphur bases*, are usually the protosulphurets of electro-positive metals, and therefore correspond to the alkaline bases of those metals ; and the electro-negative sulphurets, *sulphur-acids*, are the sulphurets of electro-negative metals, and are proportional in composition to the acids which the same metals form with oxygen. Hence, if the sulphur of a sulphur-salt were replaced by an equivalent quantity of oxygen, an oxy-salt would result. Thus bisulphuret of carbon, a sulphur-acid, unites with sulphuret of potassium, a sulphur-base, forming the sulphur-salt $KS + CS_2$. Now if the sulphur of this compound be replaced by oxygen, we have the carbonate of potassa, $KO + CO_2$. (An. de Ch. et Ph. xxxii. 60.)

The compounds which Berzelius has enumerated as sulphur-acids are the sulphurets of arsenic, antimony, tungsten, molybdenum, tellurium, tin, and gold. To these he has added the sulphurets of several other substances not metallic, such as sulphuret of selenium, bisulphuret of carbon, and the hydrosulphuric and hydrosulphocyanic acids. He mentions also, that just as two electro-positive oxides may combine, one becoming electro-negative in regard to the other, so may a sulphur-salt be generated by the union of electro-positive sulphurets.

The native double sulphuret of copper and iron, and a considerable number of similar compounds, are instances of this nature. These analogies are rendered much closer by the facts that hydrosulphuric and hydrosulphocyanic acids act as hydro-acids with ammonia, and as sulphur-acids with sulphur-bases; and that all the sulphurets which are remarkable as *sulphur-acids*, have likewise the property of combining with ammonia.—I shall accordingly place the double sulphurets as a third order of the class of salts, and describe them under the name of sulphur-salts.

A fourth order of salts has been formed by Berzelius, comprising for the most part bi-elementary compounds, which consist of a metal on the one hand, and of chlorine, iodine, bromine, fluorine, and the radicals of the hydracids on the other. He has applied to them the name of *haloid-salts* (from ἅλς sea-salt, and ειδος form), because in constitution they are analogous to sea-salt. The whole series of the metallic chlorides, iodides, bromides, and fluorides, such as chloride of sodium, iodide of potassium, and fluor-spar, as well as the cyanurets, sulphocyanurets, and ferrocyanurets, are included in his list of haloid-salts. (An. de Ch. et Ph. xxxii. 60.) The reader will at once perceive that these haloid-salts, as bi-elementary compounds, differ in composition from other salts, and are analogous to oxides and sulphurets. But their characters are essentially those of the oxygen salts. Thus, chloride of sodium, or sea-salt, is very similar in its properties to sulphate or nitrate of soda. Indeed, the generic term *salt* is taken from sea-salt.

The preceding pages contain an account of the different classes of compounds which have been termed salts. But since the sixth edition of this work was published, new views on this important class of bodies have begun to prevail. The researches of Graham on the phosphates, those of Liebig on the constitution of the organic acids and their salts, and the experiments of Dumas, Clark, Frémy, Thaulow, Péligot, and many others, have gradually converged to the point of recalling to the recollection of chemists certain profound views, first suggested by Davy in regard to chloric and iodic acids and their salts, and afterwards applied (apparently without previous knowledge of what Davy had done) by Dulong to the salts of oxalic acid. These views have the inestimable advantage of uniting all acids into one series, and all salts into another; nay, these two series may even be considered as one. I shall here briefly explain them; but in describing the salts individually, I shall retain the usual views of the constitution of acids and salts, as the former have been thus described in the preceding part of this volume, and the chemical world is not yet ripe for a complete change in the theory of salts. The new views, however, are making such rapid progress, and are so closely entwined with the details of every part of chemistry, that a knowledge of them is indispensable to the student.

In regard to acids, then, the first point to be noticed is, that all so-called oxygen acids, in the free, or what may be called the *active* state, contain hydrogen. On referring to the description of the mineral acids it will be found, for example, that they are described as combining with water when separated from their combinations. Oil of vitriol is SO_3,HO; nitric acid NO_5,HO, &c. The latter, indeed, cannot exist in the supposed anhydrous state, NO_5; and this is the case with a large majority of all known acids. Sulphuric acid and phosphoric acid, no doubt, may be obtained anhydrous, SO_3 and PO_5; but it is worthy of especial notice, that in this state *they do not possess the properties of these acids*, and only acquire them on the addition of water. The compound of dry sulphuric acid and ammonia, SO_3,NH_3, *is not* sulphate of ammonia, but a distinct compound. Moreover, these anhydrous acids combine with water with the greatest vehemence, and then assume their active characters. The principal exceptions are carbonic acid and chromic acid; but, on the other hand, none of the organic acids can exist without water, that is, without hydrogen.

It is obvious that hydrogen is essential to the hydracids. Now the view which I wish here to explain considers both these classes of acids as hydracids, and thus unites in one class or series bodies having the most perfect analogy in properties. According to this view, therefore, the general formula of a hydracid is $X + H$; X being an acid-radical, which may be either simple or compound. Thus in hydrochloric, hydriodic, and hydrosulphuric acids respectively, X is represented by Cl, I, or S. In hydrocyanic and hydrosulphocyanic acids, X is represented by $Cy = C_2N$, and by $CyS_2 = C_2NS_2$, respectively.

In the hydrated oxygen acids of the preceding pages, to which alone, and not to the anhydrous acids, this theory applies, X is always a compound, and always contains oxygen. Thus in hydrated sulphuric acid, commonly so called, and represented by SO_3,HO, X is represented by SO_4; in nitric acid, NO_5,HO, $X = NO_6$; and in metaphosphoric acids, PO_5,HO, $X = PO_6$: and the true formulæ of these acids are SO_4,H, NO_6,H, and PO_6,H, respectively.

Further, among the organic acids to be afterwards described, we find a corresponding constitution. In acetic acid (hydrated) $C_4H_3O_3,HO$, $X = C_4H_3O_4$; in hydrated formic acid, C_2HO_3,HO, $X = C_2HO_4$, &c.

The next point to be noticed is, that acids exist, the general formula of which is $X + H_n$; that is, in which X combines with two or more equivalents of H, and which are called polybasic acids. Those acids, above described, in which there is 1 eq. of H, are called monobasic acids. Where 2 eq. of H are present the acid is bibasic; with 3 eq. of H, tribasic, and so on. The reason of this nomenclature will appear when we come to salts.

Examples of this kind are, pyrophosphoric acid, $PO_5,2HO$, which is bibasic, its true formula being PO_7,H_2; phosphoric acid, $PO_5,3HO$, which is a tribasic acid, PO_8,H_3; and arsenic acid, $AsO_5,3HO$; also a tribasic acid, AsO_8,H_3.

But it is among the organic acids that we find the most numerous and striking examples of polybasic acids. The following table contains the formulæ of some of these:—

Meconic Acid . .	$C_{14}H\ O_{11}+3HO$(tribasic)$=C_{14}H\ O_{14}+H_3$.
Cyanuric Acid . .	$Cy_3\ O_3+3HO$(tribasic)$=Cy_3\ O_6+H_3$.
Citric Acid . .	$C_{12}H_5O_{11}+3HO$(tribasic)$=C_{12}H_5O_{14}+H_3$.
Tannic Acid . .	$C_{18}H_5O_9+3HO$(tribasic)$=C_{18}H_5O_{12}+H_3$.
Tartaric Acid . .	$C_8\ H_4O_{10}+2HO$(bibasic)$=C_8\ H_4O_{12}+H_2$.
Komenic Acid . .	$C_{12}H_2O_8+2HO$(bibasic)$=C_{12}H_2O_{10}+H_2$.
Fulminic Acid . .	$Cy_2\ O_2+2HO$(bibasic)$=Cy_2\ O_4+H_2$.
Mucic Acid . .	$C_{12}H_8O_{12}+2HO$(bibasic)$=C_{12}H_8O_{16}+H_2$.

Moreover there are also polybasic acids which contain no oxygen, analogous in this respect to hydrochloric and hydrocyanic acids. Thus, ferrocyanic acid is represented by Cy_3Fe+H_2; and ferridcyanic acid is $Cy_6Fe_2+H_3$.

It will be obvious at a glance, that this theory of acids possesses the advantages of simplicity and of uniting in classification a vast number of bodies, similar in properties, which have formerly been arbitrarily separated. But the chief advantage attending it is, that it enables us to effect the same union into one class of all the salts of the acids containing hydrogen. It is in examining the salts, moreover, that we find the strongest arguments in favour of the theory as applied to acids.

A salt is formed, whenever one of these acids is neutralized by a metallic oxide, by ammonia, or by an organic base, or combines with them, without being neutralized.

Now, when a salt is thus formed, one phenomenon constantly occurs; this is the separation of *water*. In the simplest case, namely, where the hydracid of an elementary body acts on a metallic protoxide, the origin of the water is quite obvious. When hydrochloric acid, for example, acts on oxide of silver, chloride of silver is formed, and water is eliminated: $HCl+AgO=AgCl+HO$. There is here no doubt that the water is produced by the reaction.

But when hydrated sulphuric acid acts on the same oxide, although the phenomena are exactly the same, a different explanation is commonly given; and the water is assumed to have pre-existed in the acid, thus, $SO_3,HO+AgO=SO_3,AgO+HO$.

It is contrary to all sound principles of reasoning to adopt two explanations of facts precisely similar: where one will suffice, and, in this case, only one explanation of the former case is possible, we must apply the same explanation to the latter. This is done by the new theory; and the following formulæ will show the identity of the reaction in the two cases:—

$$\begin{gathered} H,Cl+Ag,O=Ag,Cl+H,O. \\ H,SO_4+AgO=Ag,SO_4+HO. \end{gathered}$$

In both cases the water is formed by the union of the hydrogen of the acid with the oxygen of the oxide; and consequently in both cases the hydrogen of the acid has been replaced by the metal.

Here, then, is the theory of salts. A salt is formed when the replaceable hydrogen of the acid is replaced by its equivalent of a metal. Consequently, acids may be viewed as the hydrogen salts of their radicals, and thus acids and salts, in regard to their constitution, will form but one class.

As the metals replace hydrogen equivalent for equivalent, it is obvious that polybasic acids will form polybasic salts. This has already been illustrated under phosphoric acid, but other examples may be given. Thus, when cyanuric acid acts on oxide of silver, 3 atoms of the latter are required for one of the former, $(Cy_3O_6+H_3)+3AgO=(Cy_3O_6+Ag_3)+3HO$. With fulminic acid 2 atoms are required, $(Cy_2O_4+H_2)+2AgO=(Cy_2O_4+Ag_2)+2HO$. It is unnecessary here to multiply these examples.

One remarkable consequence, deducible from the theory under consideration is, that those oxides which most easily lose oxygen should most readily replace by their metal the hydrogen of the acid. This is found to be the case. For example, potash can only replace by potassium 2 of the 3 eq. of hydrogen in cyanuric acid, and 1 of the 2 eq. of hydrogen in fulminic acid, forming the compounds $Cy_3O_6\left.\begin{matrix}K_2\\H\end{matrix}\right\}$ and $Cy_2O_4\left.\begin{matrix}K\\H\end{matrix}\right\}$, while with oxide of silver, an easy reducible oxide, the replacement, as before mentioned, is complete. This fact furnishes an almost irresistible argument for the existence of hydrogen, as such, in acids; and further explains the formerly unaccountable fact, that the neutral salts formed by the action of oxide of silver on organic acids are always anhydrous. In the case of phosphoric and arsenic acids, also, oxide of silver forms anhydrous salts, or, in other words, replaces the hydrogen entirely, with much greater facility than potash or soda.

Another obvious consequence of this theory is, that the neutralizing power of an acid depends entirely on the number of equivalents of hydrogen replaceable by metals. Take, for example, hydrosulphuric acid, $S + H$, and add to the radical oxygen, &c., in almost any proportion; the neutralizing power remains unchanged, as the following table shows:—

	X=	
Hydrosulphuric Acid	$S + H.$	
Sulphurous Acid	$SO_3 + H.$	
Sulphuric Acid	$SO_4 + H.$	
Hyposulphurous Acid	$S_2O_3 + H.$	
Hyposulphuric Acid	$S_2O_6 + H.$	
Hydrosulphocyanic Acid	$S_2Cy + H.$	
Chlorosulphuric Acid	$SO_3Cl + H.$	(Regnault.)
Nitrosulphuric Acid	$SNO_5 + H.$	(Pelouze.)

No substances can be more different in composition than the above, yet they all neutralize exactly the same quantity of base; a fact readily explained, when it is considered that neutral salts result from the complete replacement of the hydrogen by metals.

The salts of ammonia form no exception to our theory. They always contain 1 at. of water, essential to their existence. Thus, sulphate of ammonia, anhydrous, contains $SO_3,NH_3,HO = SO_3,NH_4O = SO_4 + NH_4$. In this last formula, NH_4 represents the supposed metal ammonium, which, if it be a metal, only differs from ordinary metals in being compound, just as cyanogen, a compound acid-radical, differs from chlorine.

I shall resume this subject when treating of the organic acids; and meantime I return to the description of the salts, according to the views still prevailing, with which the student must also make himself well acquainted, as they pervade all chemical works.

Consistently with the views developed in the first part of this section, I have grouped together all saline compounds which have a certain similarity of composition into one great class of *salts*, which is divided into the four following orders:—

Order I. The oxy-salts. This order includes no salt the acid or base of which is not an oxidized body.

Order II. The hydro-salts. This order includes no salt the acid or base of which does not contain hydrogen.

Order III. The sulphur-salts. This order includes no salt the electro-positive or negative ingredient of which is not a sulphuret.

Order IV. The haloid-salts. This order includes no salt the electro-positive or negative ingredient of which is not haloidal.

The nomenclature of the first order of salts was explained on a former occasion. The insufficiency of the division into *neutral*, *super*, and *sub*-salts, will be made apparent by the following remarks. In the first place, some alkaline bases form more than one super-salt, in which case two or more different salts would be included under the same name. Secondly, some salts have an acid reaction, and might therefore be denominated super-salts, although they do not contain an excess of acid. Nitrate of oxide of lead, for instance, has the property of reddening litmus paper; whereas it consists of 1 eq. of oxide of lead and 1 eq. of nitric acid, and therefore in composition is precisely analogous to nitrate of potassa, which is a neutral salt. This fact was noticed some years ago by Berzelius, who accounted for the circumstance in the following manner:—The colour of litmus is naturally red, and it is only rendered blue by the colouring matter combining with an alkali. If an acid be added to the blue compound, the colouring matter is deprived of its alkali, and thus, being set free, resumes its red tint. Now on bringing litmus paper in contact with a salt, the acid and base of which have a weak attraction for each other, it is possible that the alkali contained in the litmus paper may have a stronger affinity for the acid of the salt than the base has with which it was combined; and in that case the alkali of the litmus being neutralized, its red colour will necessarily be restored. It is hence apparent that a salt may have an acid reaction without having an excess of acid.

The nomenclature of the hydro-salts is framed on the same principles as that applied to the salts which contain oxygen. With respect to the third and fourth orders of salts, no general principle of nomenclature has yet been agreed on. Berzelius has extended to them the same nomenclature which he employs for the oxy-salts, and some chemists seem disposed to follow his example; but as new views are apt to be obscured, and their intrinsic value overlooked, by being expressed in new language, I shall confine myself as much as possible to terms with which every chemist is familiar. It is worthy of consideration whether the nomenclature of the sulphur and haloid salts, instead of being purposely assimilated to that of the other salts, should not designedly be kept distinct, in order the more readily to distinguish between analogous compounds.

Nearly all salts are solid at common temperatures, and most of them are capable of crystallizing. The colour of salts is very variable, having no necessary connexion with the colour of their elements. Salts composed of a colourless acid and base are colourless; but a salt, though formed of a coloured oxide or acid, may be colourless; or, if coloured, the tint may differ from that of both its constituents.

All soluble salts are more or less sapid, while those that are insoluble in water are insipid. Few salts are possessed of odour: the most remarkable one for this property is carbonate of ammonia.

Salts differ remarkably in their affinity for water. Thus some salts, such as the nitrates of lime and magnesia, are *deliquescent*, that is, attract moisture from the air, and become liquid. Others, which have a less powerful attraction for water, undergo no change when the air is dry, but become moist in a humid atmosphere; and others may be exposed without change to an atmosphere loaded with watery vapour.

Salts differ likewise in the degree of solubility in water. Some dissolve in less than their weight of water; while others require several hundred times their weight of this liquid for solution, and others are quite insoluble. This difference depends on two circumstances, namely, on their affinity for water, and on their cohesion; their solubility being in direct ratio with the first, and in inverse ratio with the second. One salt may have a greater affinity for water than another, and yet be less soluble; an effect which may be produced by the cohesive power of the salt which has the stronger attraction for water being greater than that of the salt which has a less powerful affinity for that liquid. The method proposed by Gay-Lussac for estimating the relative degrees of affinity of salts for water (An. de Ch. lxxxii.) is by dissolving equal quantities of salts in equal quantities of water, and applying heat to the solutions. That salt which has the greatest affinity for the menstruum will retain it with most force, and will therefore require the highest temperature for boiling.

Salts which are soluble in water crystallize more or less regularly when their solutions are evaporated. If the evaporation is rendered rapid by heat, the salt is usually deposited in a confused crystalline mass; but if it take place slowly, regular crystals are formed. The best mode of conducting the process is to dissolve a salt in hot water, and when it has become quite cold to pour the saturated solution into an evaporating basin, which is to be set aside for several days or weeks without being moved. As the water evaporates, the salt assumes the solid form; and the slower the evaporation, the more regular are the crystals. Some salts which are much more soluble in hot than in cold water, crystallize with considerable regularity when a boiling saturated solution is slowly cooled. The form which salts assume in crystallizing is constant under the same circumstances, and constitutes an excellent character by which they may be distinguished from one another.

Many salts during the act of crystallizing unite chemically with a definite portion of water, which forms an essential part of the crystal, but not of the salt, and is termed *water* of *crystallization.* The quantity of combined water is very variable in different saline bodies, but is uniform in the same salt. A salt may contain more than half its weight of water, and yet be quite dry. On exposing a salt of this kind to heat, it is dissolved, if soluble, in its own water of crystallization, undergoing what is termed the *watery fusion.* By a strong heat the whole of the water is expelled; for no salt can retain its water of crystallization when heated to redness. Some salts, such as sulphate and phosphate of soda, lose a portion of their water, and crumble down into a white powder, by mere exposure to the air; a change which is called *efflorescence.* The tendency of salts to undergo this change depends on the dryness and coldness of the air; for a salt which effloresces rapidly in a moderately dry and warm atmosphere, may often be kept without change in one which is damp and cold.

The water of crystallization is retained by a very feeble affinity, as is proved by the phenomena of efflorescence, and by the facility with which such water is separated from the saline matter by a moderate heat, or by exposure to the vacuum of an air-pump at common temperatures. It is frequently observed, however, that a portion of the water is retained with such obstinacy that it cannot be expelled by a temperature short of that at which the salt is totally decomposed. This water, as in the case of the hydrated acids, is considered to act the part of a base, and is hence commonly called basic water, as has already been explained in the section on phosphorus. But from the observations of Graham it would appear that the water thus retained does not always act the part of a base, but is in a peculiar state of combination characteristically different both from basic water and water of crystallization. (Ph. Tr. Ed. xii. 297.) In his original paper he distinguished it as saline water; but in a report read to the meeting of the British Association in Liverpool, he has called it constitutional water. It is readily distinguished from water of crystallization, by being retained by a stronger affinity, and by being essential to the existence of the salt of which it constitutes a part. From basic water it differs by not being removed from its combinations even by the most powerful alkalies, whereas it is readily removed, and its place in the compound assumed, by certain anhydrous salts: it is also expelled from an acid more readily than the basic water. From an example the character of water in these different states of combination will be readily understood. The crystals of the common phosphate of soda are composed of 1 eq. of phosphoric acid, 2 eq. of soda, and 25 eq. of water. On exposing them to a temperature of 212°, 24 eq. of the water are readily expelled; but the 25th eq. is retained with such power, that a red heat is necessary to effect its complete separation. By the loss of the 24 eq. of water, the crystalline form and texture of the salt is entirely destroyed, but the residual amorphous mass has all the properties of the common phosphate; whereas by the loss of the

25th, an entirely different salt, the pyrophosphate of soda, is produced. It will hence appear, that the 24 eq. of water which were lost at 212° were only essential to the existence of the crystal, while the loss of the 25th eq., which in this case is basic, affected that of the salt.

The same thing is observed in the case of sulphate of oxide of zinc. Its common crystals are composed of 1 eq. of sulphuric acid, 1 eq. of oxide of zinc, and 7 eq. of water, six of which are readily lost at 212°, the crystal being at the same time destroyed, while the 7th eq. is not expelled until the temperature rises above 410°. Thus far the 7th eq. of water in sulphate of zinc appears analogous to the 25th in the common phosphate of soda; but Graham has pointed out the remarkable difference, that in the latter salt the eq. of water is readily removed from its combination by an eq. of any base which supplies its place in the compound; while in sulphate of zinc, the 7th eq. of water is not affected by bases, but may be removed by anhydrous sulphates, which occupy its place and give rise to the formation of double salts. The former, as acting the part of a base, is called basic water; the latter, as influencing the constitution of a salt, is called constitutional water. The difference is denoted in symbols, by writing the basic water, as is the case with all bases, on the left side of the acid with which it is combined, and the constitutional water on the right. Hence the symb. of the crystals of phosphate of soda is $2NaO,HO.\ P_2O_5 +$ 24 aq.; and of the sulphate of zinc, $ZnO\ SO_3,\ HO + 6$ aq. In the phosphate the water may be removed by soda, forming $3NaO.\ P_2O_5 +$ 24 aq.; in the sulphate, by anhydrous sulphate of potassa, forming the double salt $ZnO\ SO_3\ (KO\ SO_3)$.

In pursuing the study of this subject, Graham has been led to the conclusion that all salts are neutral in their constitution with the exception of certain classes. Thus he finds that the bisulphate of potassa is a double salt, formed by the constitutional water of sulphate of water being replaced by sulphate of potassa; thus

$$\begin{array}{l} HO\ SO_3,HO \\ \text{and } KO\ SO_3 \end{array} \ \text{yield}\ \begin{array}{l} HO\ SO_3,\ (KO\ SO_3) \\ \text{and } HO. \end{array}$$

To illustrate the constitution of a sub-salt, the nitrates were selected. Nitric acid of sp. gr. 1·42 he considers to be nitrate of water with 3 eq. of constitutional water; its symb. is therefore $HO\ NO_5.\ 3HO$. But water corresponds with the class of isomorphous oxides of which magnesia, the oxides of zinc or of copper, may be taken as the type. Hence these oxides are capable of supplying the place of water in either state of combination, as is seen in the neutral and sub-nitrate of copper, in the former of which the basic water is replaced by an eq. of oxide of copper, while in the sub-salt the 3 eq. of constitutional water are replaced by 3 eq. of oxide of copper. Their constitution is therefore represented by the formulæ

$$CuO\ NO_5 .\ 3HO,$$
$$\text{and } HO\ NO_5 .\ 3Cu\ O.$$

In applying these views in other cases, however, difficulties arise, owing to the existence of anhydrous bisalts, as the anhydrous bisulphate and bichromate of potassa. These are accounted for by Graham, by supposing the existence of a class of bodies, called by him basic adjuncts, which admit of being attached to the oxide of hydrogen, or to the oxides of metals—the only true bases. The arguments in support of this view are principally drawn from the composition of the ammoniacal salts: it must be remembered, however, that the whole subject is in many respects hypothetical, and has not yet been sufficiently tested by experiment.

Salts, in crystallizing, frequently enclose mechanically within their texture particles of water, by the expansion of which, when heated, the salt is burst with a crackling noise into smaller fragments. This phenomenon is known by the name of *decrepitation.* Berzelius has correctly remarked that those crystals decrepitate most powerfully, such as the nitrates of baryta and oxide of lead, which contain no water of crystallization.

The atmospheric pressure is said to have considerable influence on the crystallization of salts. If, for example, a concentrated solution, composed of about three parts of sulphate of soda in crystals, and two of water, is made to boil briskly, and the flask which contains it is then tightly corked, while its upper part is full of vapour, the solution will cool down to the temperature of the air without crystallizing, and may in that state be preserved for months without change. Before removal of the cork, the liquid may often be briskly agitated without losing its fluidity; but on readmitting the air, crystallization commonly commences, and the whole becomes solid in the course of a few seconds. The admission of the air sometimes, indeed, fails in causing the effect; but it may be produced with certainty by agitation or the introduction of a solid body. The theory of this phenomenon is not very apparent. Gay-Lussac has shewn that it does not depend on atmospheric pressure (An. de Ch. vol. lxxxvii.); for he finds that the solution may be cooled in open vessels without becoming solid, provided its surface be covered with a film of oil; and I have frequently succeeded in the same experiment without the use of oil, by causing the air of the flask to communicate with the atmosphere by means of a moderately narrow tube. It appears from some experiments of Graham (Phil. Trans. Edin., 1828), that the influence of the air may be ascribed to its uniting chemically with water; for he has proved that gases which are more freely absorbed than atmospheric air, act more rapidly in producing crystallization. Indeed, the rapidity of crystallization, occasioned by the contact of gaseous matter, seems proportional to the degree of its affinity for water.

The same quantity of water may hold several different salts in solution, provided they do not mutually decompose each other. The solvent power of water with respect to one salt is, indeed, sometimes increased by the presence of another, owing to combination taking place between the two salts.

Most salts produce cold during the act of solution, especially when they are dissolved rapidly and in large quantity. The greatest reduction of temperature is occasioned by those which contain water of crystallization.

All the oxy-salts are decomposed by voltaic electricity, provided they are either moistened or in solution. The acid appears at the positive pole of the battery, and the oxide at its opposite extremity; or, if the oxide is of easy reduction, the metal itself goes over to the negative side, and its oxygen accompanies the acid to the positive wire.

The hydro-salts, and doubtless also the sulphur and haloid-salts, are subject to a similar change; but the phenomena as respects the two last orders of salts have been little examined.

ON CRYSTALLIZATION.

The particles of liquid and gaseous bodies, during the formation of solids, sometimes cohere together in an indiscriminate manner, and give rise to irregular shapeless masses; but more frequently they attach themselves to each other in a certain order, so as to constitute solids possessed of a symmetrical form. The process by which such a body is produced is called *crystallization;* the solid itself is termed a *crystal;* and the science, the object of which is to study the form of crystals, is *crystallography.*

Most bodies crystallize under favourable circumstances. The condition by which the process is peculiarly favoured is the slow and gradual change of a fluid into a solid, the arrangement of the particles being at the same time undisturbed by motion. This is exemplified during the slow cooling of a fused mass of sulphur or bismuth, or the spontaneous evaporation of a saline solution; and the origin of the numerous crystals, which are found in the mineral kingdom, may be ascribed to the influence of the same cause.

All substances are limited in the number of their crystalline forms.

Thus, calcareous spar crystallizes in rhombohedrons, fluor-spar in cubes, and quartz in six-sided pyramids; and these forms are so far peculiar to those substances, that fluor-spar never crystallizes in rhombohedrons or six-sided pyramids, nor calcareous spar or quartz in cubes. Crystalline form may therefore serve as a ground of distinction between different substances. It is accordingly employed by mineralogists for distinguishing one mineral species from another; and it is very serviceable to the chemist as affording a physical character for salts. On this account I have thought it would be useful, before describing the individual salts, to introduce a few pages of crystallization; but from the great extent of the subject, which now constitutes a separate science, my remarks must necessarily be limited, and comprehend little else than a brief outline of its more important principles. To those who are desirous of more ample information, I may recommend the "Elements of Crystallography," by Gustav. Rose; or Mr. Whewell's Essay in the Phil. Trans. of London for 1825.

Every perfect crystal is bound by plane surfaces, which are called its faces. The straight line formed by the intersection of two faces is called an edge; the meeting of three or more edges in a point forms a solid angle. Thus in the octohedron, fig. 1, the bounding planes are the faces, the lines formed by their intersection the edges, the meeting of four of which in the same point produces a solid angle of the crystal.

The forms of crystals are exceedingly diversified. They are divided by crystallographers into simple and compound; a simple form has all its faces equal and similar to each other, while a compound form is bounded by at least two different classes of faces. Thus, figs. 1, 2, and 3 are simple forms; for the first is bounded by eight faces, each of which is an equilateral triangle, the second by six squares, and the third by twelve equal and similar rhombi. The forms represented by

Fig. 1.

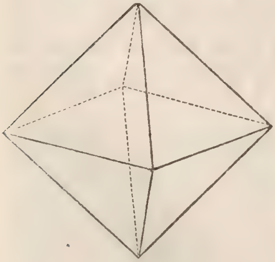


Fig. 2.

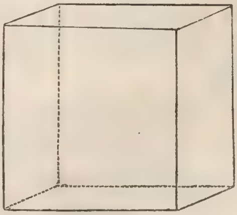
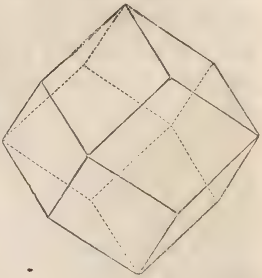


Fig. 3.



4, 5, and 6 are, on the contrary, compound crystals: for fig. 4 is composed of two classes of faces, eight of which are hexagonal, and six square; while fig. 6 contains three classes, eight faces being hexagonal, six octagonal, and twelve quadratic. This division into compound and simple is not artificial, but is founded on the fact that the compound forms are really produced by the combination of two or more of the simple crystals, as will be seen by a careful inspection of the forms and relative situations of the faces in the accompanying figures. The character of the faces in figures 1, 2, and 3, which represent respectively the regular octohedron, the cube, and the rhombic dodecahedron, is too obvious to demand comment; but to obtain a correct idea of the relative positions of the faces in these three forms requires a more careful investigation.

Fig. 4.

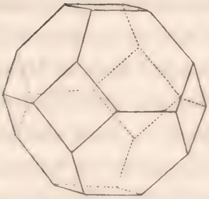


Fig. 5.

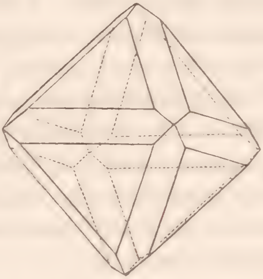
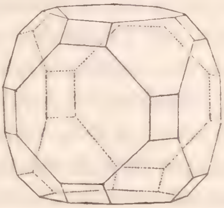


Fig. 6.



It will be observed that in each of these figures three right lines, which are equal in length, perpendicular to each other, and pass through the centre of the crystal, may be obtained;—in the octohedron by joining the opposite angles, in the cube by joining the centres of the opposite faces, and in the rhombic dodecahedron by connecting the opposite angles formed by the meeting of four edges, these angles being six in number and corresponding in situation to the six angles of the octohedron. The lines around which the different parts of the crystals are thus symmetrically grouped are called crystalline axes. Hence the above forms are connected by being possessed of the same axes of crystallization, and proceeding from these three equal and rectangular axes, either the octohedron, the cube, or the rhombic dodecahedron may be constructed, the resulting form being solely dependent on the law in accordance with which planes are symmetrically arranged or grouped around the axes. The octohedron (fig. 1) results from the law that every plane shall pass through an extremity of each axis: it will be evident that one, and only one plane, fulfilling the required condition, may be introduced into each of the eight octants formed by the intersection of the three axes. This law, therefore, limits the number of faces to eight; and as these intersect each other in the lines joining the extremities of the axes, each face is an equilateral triangle, and the resulting form is the regular octohedron. The cube (fig. 2) results from the law that each plane shall pass through an extremity of one axis, and be parallel to the other two: as each of the three axes has two extremities, six, and only six, planes can be grouped around them in accordance with this law, and by their intersection the hexahedron, or cube, as it is more commonly called, is produced. In a similar manner may the rhombic dodecahedron (fig. 3) be shewn to be formed according to the law that each plane shall pass through the extremities of two axes, and be parallel to the third.

The groups of simple forms, which are thus associated by being reducible from the same axes, constitute what is called by crystallographers a system of crystallization. Thus the octohedron, the cube, and the rhombic dodecahedron are three forms of what is called the octohedral or regular system. Such forms are associated not merely by the similarity of their axes, but are connected still more intimately by the remarkable fact, that any substance which in crystallizing assumes one form of a system, may, and frequently does, assume other forms belonging to that system. Examples of this may be seen in the well-known salt alum, and in the black oxide of iron, the magnetic ore of mineralogists; the former generally crystallizing in the octohedron (fig. 1), but it may also be obtained in the form of the cube (fig. 2); and the magnetic iron ore is found not only in the form of octohedrons and cubes, but likewise in that of the rhombic dodecahedron (fig. 3). But, what is still more remarkable, the same substance is not only capable of assuming different forms of the same system, but during the act of crystallization the faces of two, three, four, and in some cases even more, of these forms are simultaneously developed, whereby compound crystals of the greatest diversity of form and appearance are produced. Thus, in crystallization of alum either the cube or octohedron may be formed, but it is by far more common that the faces of both be produced, giving rise to the compound crystal represented in fig. 4, where the faces of the cube appear truncating the angles of the octohedron. Another form frequently observed in alum is represented by fig. 5, where, in addition to the octohedron, the faces of the rhombic dodecahedron are also developed; and as these are twelve in number, and correspond in situation to the twelve edges of the octohedron, their development removes, or as it is technically expressed, truncates the twelve edges of the latter form. Fig. 6 represents a combination of all three forms. Similar and still more complicated combinations are observed on magnetic iron ore.

The importance of a knowledge of all the simple forms of a system, as being those in which the same substance may occur, and which alone can give rise to compound crystals, for simple forms of different systems are never combined, will be felt from what has already been stated. The first person who proved the existence of a mathematical connection between them was the celebrated crystallographer Haüy; but it is to Weiss, Professor of Mineralogy in Berlin, that we are indebted for the distinction of the systems of crystallization,—a discovery which justly entitles him to the honour of being the founder of modern crystallography. He has shewn that all crystalline forms may be brought under one of the six following systems, which may be conveniently distinguished as,

1. The octohedral, or regular system of crystallization.
2. The square prismatic ditto ditto.
3. The right prismatic ditto ditto.
4. The oblique ditto ditto.
5. The doubly oblique ditto ditto.
6. The rhombohedral system ditto ditto.

The Octohedral System.—This system is characterized by the three equal and rectangular axes, which have already been described. Let them be distinguished as the axes *a*, *b*, and *c*; and, for the convenience of reference, let us consider that the figure be brought into such a position that two of them, *a* and *b*, be horizontal, and *c* vertical. The figs. 1, 2, and 3 are drawn under this supposition. The law of crystalline symmetry, in this system, is such, that if a face of a crystal be observed to bear a certain relation to one of the axes *a*, other faces must fulfil the same condition to the equal axes *b* and *c*. Thus, if a plane be seen to pass through the extremity of *a*, or be parallel to it, other planes must pass through the extremity of *b* and *c*, or be parallel to them. Owing to the perfect symmetry in the different parts of the crystal, this group is frequently called the regular system of crystallization.

It consists of but few simple forms, the number being necessarily limited to the number of different ways in which a plane can intersect the three axes. These, it will be seen, are only seven:—

1. The plane may cut each at an equal distance from the centre. The crystal the faces of which obey this law is the octohedron, fig. 1.

2. The plane may cut two axes at an equal, and the third at a

greater distance from the centre. The resulting form is called the triakisoctohedron.

3. The plane may cut two axes at an equal, and the third at a less distance from the centre. The resulting form is the ikositetrahedron.

4. The plane may cut all three axes unequally. The form is the hexakisoctohedron.

5. The plane may cut two axes at unequal distances from the centre, and be parallel to the third. The resulting crystal is the tetrakishexahedron.

6. The plane may cut two axes in points equally distant from the centre, and be parallel to the third. The form is the rhombic dodecahedron, fig. 3.

7. The plane may cut one axis, and be parallel to the other two. This law gives rise to the cube or hexahedron, fig. 2.

Of these forms 1, 6, and 7 are of frequent occurrence; but the others are usually found only in combination, when their faces are generally small, and appear symmetrically arranged around the angles and on the edges of the former. Hence, in most compound crystals of this system, the faces either of the octohedron, cube, or rhombic dodecahedron may be readily recognized; and as these suffice to fix the position of the crystalline axes, they serve as a guide to determine the forms of the combination. Their prevalence presents also a remarkable instance of the tendency to simplicity which may be observed in all the processes of nature. This is not only seen in the greater simplicity of exterior form, but in the more definite nature of the laws by which the faces of these three crystals are determined; for while a plane has but one position in which it can satisfy the laws 1, 6, and 7, an unlimited number of planes may be found to satisfy the conditions expressed by 2, 3, 4, and 5. Thus, for example, there is but one way in which a plane can satisfy the law 1; while there are as many ways of satisfying the law 4, as there are of taking three lines which shall be unequal. Hence it follows that there can be but one octohedron, while the number of hexakisoctohedrons is unlimited, and the faces of two different ones have been observed on the same crystals. The latter observation also applies to the forms produced according to the laws 2, 3, and 5; but the number of varieties which have been observed is very limited, and the relative lengths of the unequal axes may be expressed, almost without an exception, by the numbers 1, $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, and $\frac{1}{5}$.

It is frequently observed in crystals of this system, that one-half of the faces of the crystals are much more developed than the other. This may be seen in figure 7, a crystal of the red oxide of copper, where four out of the eight faces of the octohedron have increased, and the other four proportionally diminished. The faces which increase, as well as those which diminish, always form two similar and symmetrically arranged groups, the increasing faces or groups of faces touching each other at the angular points of the crystal. Thus, in the octohedron, the four alternating faces which do not intersect in edges, but merely touch each other in the angular points, increase, as represented in figure 7, and by increasing till they form a perfect figure, give rise to the well-known crystal the tetrahedron, fig. 8. These forms are called hemihedral, as denoting their origin: hence the tetrahedron is commonly known as the hemi-octohedron. Each of the simple forms of this system, with the exception of the cube and rhombic dodecahedron, gives rise to hemihedral crystals: the exception evidently results from the impossibility of dividing the faces of the cube and rhombic dodecahedron into two groups, which fulfil the necessary conditions.

Fig. 7.

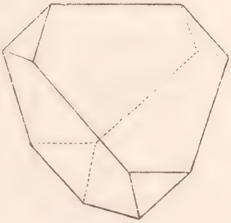
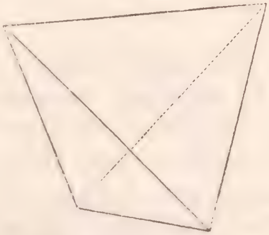
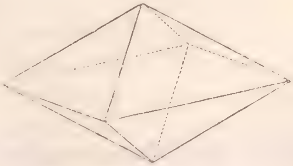


Fig. 8.



The Square Prismatic System.—The forms of this system are, like those of the preceding, characterized by three axes, which intersect each other at right angles; but they differ from them by two only out of the three being equal. Let the third, which may be either greater or less than the two equal axes, be called c, and let it be placed in a vertical position. The octohedron formed by joining the extremities of these axes, is either longer or shorter in the direction of the axis c than in that of its horizontal axes, as is seen in fig. 9. From this it follows that these octohedrons may be compared to a double four-sided pyramid constructed on either side of a square base. The parts of the crystal about this base are therefore similar to each other, but differ from those about its upper or lower extremity; and as this observation applies equally to all forms of this system, it is the character by which the system is best distinguished.

Fig. 9.



This difference is owing to the inequality of the vertical axis, which causes the relations of the faces to it to be unconnected with those they bear to the two horizontal axes. Hence it is common to find the lateral edges truncated without those connected with the extremities of the crystal being affected, whereby a square prism terminated by four-sided pyramids, as represented in fig. 10, is produced. The same may occur on the lateral angles as well as edges, as in fig. 11. In other cases, the terminal edges and angles are modified, but always in a different manner from the lateral.

Fig. 10.

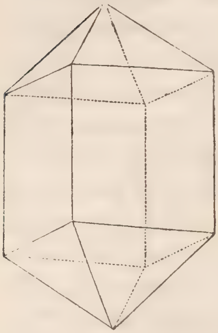
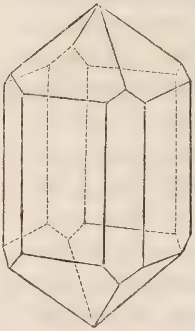


Fig. 11.



The Right Prismatic System.—The crystals of this system are, like the preceding, characterized by three rectangular axes, and are distinguished from both by no two of these axes being equal. Its forms are therefore not only distinguished by a difference in the lateral and terminal parts, but are still further marked by the difference between the front and back of the crystal, as compared with its sides. Thus, in figs. 12, 13, and 14, which represent three of the common forms of sulphur, the different magnitude in the parts of the crystals about each axis is perceptible, and sufficiently marks the different crystallographic values of the three axes. But this is still better pointed out by the three different and independent modifications of the rhombic octohedron, which forms the basis of all three crystals.

Fig. 12.

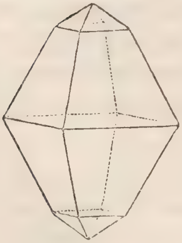


Fig. 13.

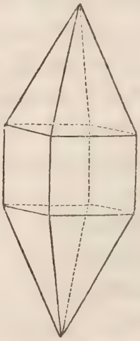
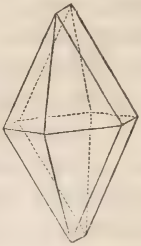
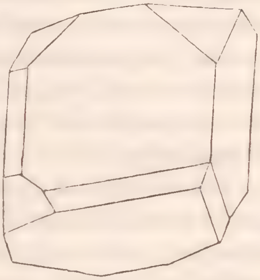


Fig. 14.



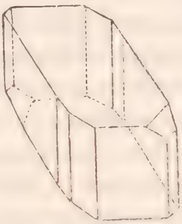
The Oblique Prismatic System.—The crystals of this system, of which an example may be seen in sulphate of the protoxide of iron, fig. 15, differ from those of the right prismatic system by the front and back parts being dissimilar. This difference is owing to two of the axes intersecting each other obliquely, while the the third still remains perpendicular to both.

Fig. 15.



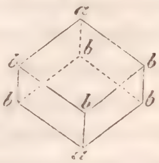
The Doubly Oblique System.—This system is readily recognized by the complete absence of all symmetry in its crystalline forms. This results from all three axes intersecting each other obliquely; owing to which the left and right sides, as well as the back and front, are of different crystallographic values. From this it follows that no two faces are connected except those which are parallel, and all symmetry of form disappears, except in the faces which are diagonally opposed and parallel, as observed in fig. 16, which represents a crystal of the sulphate of the oxide of copper.

Fig. 16.



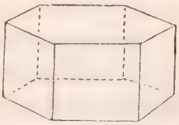
The Rhombohedral System.—The forms of this system of crystallization are, like the octohedral, characterized by three equal and similar axes; but these axes intersect each other at equal, but not at right angles. Its most simple form is the rhombohedron, fig. 17, which is bound by six equal and similar rhombic faces. The axes are obtained by joining the centre of the opposite faces. Although the faces of the rhombohedron are equal, two only of its angles, marked *a*, are regular, being formed by the meeting of three equal edges, while the other six are irregular. The line joining *a a* is called the principal axis of the rhombohedron, the angles *a* the terminal, and *b* the lateral angles of the rhombohedron.

Fig. 17.



The form which most commonly occurs associated with the rhombohedron is a hexagonal prism, fig. 18, two of which are observed, the one truncating the six angles, the other the lines joining these angles, the faces of the prism being in both cases parallel to the rhombohedral axes *a a*. The terminal angles *a* are frequently truncated by terminal planes.

Fig. 18.



The different forms of the system may be advantageously studied on crystals of quartz and calcareous spar.

Besides the distinction arising from external form, minerals are further distinguished by differences in the mechanical connexion of their particles, peculiarities which mineralogists designate by the name of *structure.* The structure of a mineral arises from its particles adhering at some parts less tenaciously than at others, and consequently yielding to force in one direction more readily than in another. Structure is sometimes visible by holding a mineral between the eye and the light; but in general it is brought into view by effecting the actual separation of parts by mechanical means.

The structure of minerals may be *regular* or *irregular.* It is regular when the separation takes place in such a manner, that the detached surfaces are smooth and even like the planes of a crystal; and it is irregular, when the new surface does not possess this character.

A mineral which possesses a regular structure is said to be *cleavable*, or to admit of *cleavage;* the surfaces exposed by splitting or *cleaving* a mineral are termed the *faces of cleavage;* and the direction in which it may be cleaved is called the *direction of cleavage.* Sometimes a mineral is cleavable only in one direction, and is then said to have a *single* cleavage. Others may be cleaved in two, three, four, or more directions, and are said to have a *double*, *treble*, *fourfold* cleavage, and so on, according to their number.

Minerals that are cleavable in more than two directions may, by the removal of layers parallel to the planes of their cleavage, be often made to assume regular forms, though they may originally have possessed a different figure. Calcareous spar, for example, occurs in rhombohedrons of different kinds, in hexagonal prisms, in six-sided pyramids, and in various combinations of these forms; but it has three sets of cleavage, which are so inclined to each other as to constitute a rhombohedron of invariable dimensions, and into that form every crystal of calcareous spar may be reduced. Lead glance possesses a treble cleavage, the planes of which are at right angles to each other; and hence it is always convertible by cleavage into the cube. The cleavages of fluor-spar are fourfold, and in a direction parallel to the planes of the regular octohedron, into which form every cube of fluor-spar may be converted.

Since the forms enumerated as belonging to the octohedral system of crystallization are possessed of fixed invariable dimensions, it is obvious that minerals, or other crystallized bodies included in that system, must often in their primary forms be identical with each other. In the other systems of crystallization this identity is not necessary, because the dimensions of their forms are variable. Thus octohedrons with a square base may be distinguished by the relative length of their axis, some being flat and others acute. Rhombic octohedrons may be distinguished from each other by the relative length of their axis, and the angles of their base. By Haüy it was regarded as an axiom in crystallography, that minerals not belonging to the octohedral system are characterized by their form ; that though two minerals may in form be analogous, each, for instance, being a rhombic prism, the dimensions of those prisms are different. Identity of form in crystals not included in the octohedral system was thought to indicate identity of composition. But in the year 1819 a discovery, extremely important both to mineralogy and chemistry, was made by Mitscherlich of Berlin, relative to the connexion between the crystalline form and composition of bodies. It appears from his researches,* that certain substances have the property of assuming the same crystalline form, and may be substituted for each other in combination without affecting the external character of the compound. Thus minerals having the crystallization and structure of garnet, and which from their appearance were believed to be such, have been found on analysis to contain different ingredients. Crystals possessed of the form and aspect of alum may be made with sulphates of potassa and peroxide of iron, without a particle of aluminous earth ; and a crystal composed of selenic acid and soda will have a perfect resemblance to Glauber's salt. The axiom of Haüy, therefore, requires an essential modification.

To the new branch of science laid open by the discovery of Mitscherlich, the term *isomorphism* (from *ισος* equal, and *μοϱφη* form) is applied ; and those substances which assume the same figure are said to be *isomorphous.* Of these isomorphous bodies several distinct groups have been described by Mitscherlich. One of the most instructive of these includes the salts of arsenic and phosphoric acid. Thus, the neutral phosphate and biphosphate of soda have exactly the same form as the arseniate and binarseniate of soda ; phosphate and biphosphate of ammonia correspond to arseniate and binarseniate of ammonia ; and the biphosphate and binarseniate of potassa have the same form. Each arseniate has a corresponding phosphate, possessed of the same form, possessing the same number of eq. of acid, alkali, and water of crystallization, and differing in fact in nothing, except that one series contains arsenic and the other an equivalent quantity of phosphorus. A second remarkable group contains the salts of sulphuric, selenic, chromic, and manganic acids. The salts of baryta, strontia, and oxide of lead constitute a third group ; and a fourth consists of lime, magnesia, and the protoxides of manganese, iron, cobalt, nickel, zinc, and copper. A fifth includes alumina, peroxide of iron, and the green oxide of chromium; and a sixth group includes the salts of permanganic and perchloric acids. In comparing together isomorphous bodies of the same group, identity of form is not to be expected unless there is similarity of composition. A neutral phosphate does not correspond to a binarseniate, nor a biphosphate to a neutral arseniate; an anhydrous sulphate is not comparable to a hydrated seleniate of the same base; nor is sulphate of protoxide of iron, with 6 eq. of water, isomorphous with sulphate of protoxide of manganese with 5 eq. In all such instances, if chemical composition differ, crystalline form is also different.

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* Annales de Ch. et de Physique, vol. xiv. 172, xix. 350, and xxiv. 264 and 355.

The following table contains a few of the principal groups of isomorphous substances at present observed by chemists: a more extended one, partly theoretical, has been drawn up by Professor Johnston, of Durham, in his Report on Chemistry to the British Association:—

1.	
Silver	$Ag.$
Gold	$Au.$
2.	
Arsenious Acid in its unusual form.	$AsO_3.$
Teroxide of Antimony	$SbO_3.$
3.	
Alumina	$Al_2O_3.$
Peroxide of Iron	$Fe_2O_3.$
Sesquioxide of Chromium	$Cr_2O_3.$
4.	
Chloride of Potassium	$KCl.$
. . Sodium	$NaCl.$
. . Lithium	$LCl.$
. . Ammonium	$NH_4,Cl.$
Bromide of Potassium	$KBr.$
. . Sodium	$NaBr.$
Iodide of Potassium	$KI.$
. . Sodium	$NaI.$
Fluoride of Potassium	$KF.$
. . Calcium	$CaF.$
5.	
Salts of	
Phosphoric Acid	$PO_5.$
Arsenic Acid	$AsO_5.$
6.	
Salts of	
Sulphuric Acid	$SO_3.$
Selenic Acid	$SeO_3.$
Chromic Acid	$CrO_3.$
Manganic Acid	$MnO_3.$
7.	
Salts of	
Perchloric Acid	$ClO_7.$
Permanganic Acid	$Mn_2O_7.$

8.	
Salts of	
Potassa	$KO.$
Ammonia with 1 eq. of water (=oxide of Ammonium $NH_4,O.$)	$NH_3,HO.$
9.	
Salts of	
Soda	$NaO.$
Oxide of Silver	$AgO.$
10.	
Salts of	
Baryta	$BaO.$
Strontia	$SrO.$
Lime (in Arrogonite)	$CaO.$
Protoxide of Lead	$PbO.$
. . Iron (in Junkerite)	$FeO.$
11.	
Salts of	
Lime	$CaO.$
Magnesia	$MgO.$
Protoxide of Iron (in Iron Spar)	$FeO.$
. . Manganese	$MnO.$
. . Zinc	$ZnO.$
. . Nickel	$NiO.$
. . Cobalt	$CoO.$
. . Copper	$CuO.$
. Lead in Plumbo-calcite	$PbO.$
12.	
Salts of	
Alumina	$Al_2O_3.$
Peroxide of Iron	$Fe_2O_3.$
Oxide of Chromium	$Cr_2O_3.$
Sesquioxide of Manganese	$Mn_2O_3.$

The preceding table will suffice to illustrate the doctrine of isomorphism, but it might be very much extended. The reader will find a very full list of crystallizable bodies, arranged according to the crystalline forms which they assume, and illustrating not only isomorphism but dimorphism, in Gmelin's Handbuch der Chemie, 4th ed., i. 83. From this table may be deduced, with others, the following groups of isomorphous elements: 1. Oxygen, sulphur, chlorine (in subchloride of copper). 2. Chlorine bromine, iodine, fluorine. 3. Carbon, phosphorus, potassium, titanium, bismuth, cadmium, lead, iron, copper, silver, and gold. 4. Potassium, sodium, lithium, calcium, zinc, lead, silver. 5. Arsenic, antimony, phosphorus, tellurium. 6. Platinum, iridium, and osmium. The groups of isomorphous compounds are very numerous, but we can here only allude to them. The circumstance that the same body occurs in two or more groups is explained by dimorphism and trimorphism, to be considered below.

The facts above mentioned afford indubitable proof that the form of crystals is materially dependent on their atomic constitution; and they at first induced Mitscherlich to suspect that crystalline form is determined solely by the number and arrangement of the atoms, quite independently of their nature. Subsequent observation, however, induced him to abandon this view; and his opinion now appears to be, that certain elements, which are themselves isomorphous, when combined in the same manner with the same substance, communicate the same form. Similarly constituted salts of arsenic and phosphoric acids yield crystals of the same figure, because the acids, it is thought, are themselves isomorphous; and as the atomic constitution of these acids is similar, each containing the same number of atoms of oxygen united with the same number of atoms of the other ingredient, it is inferred that phosphorus is isomorphous with arsenic. In like manner it is believed that selenic acid must be isomorphous with sulphuric acid, and selenium with sulphur; and the same identity of form is ascribed to all those oxides above enumerated, the salts of which are isomorphous. The accuracy of this ingenious view has not yet been put to the test of extensive observation, because the crystalline forms of the substances in question are for the most part unknown. But our knowledge, so far as it goes, is favourable; for peroxide of iron and alumina, the salts of which possess the same form, are themselves isomorphous. It may hence be inferred as probable, that isomorphous compounds in general arise from isomorphous elements uniting in the same manner with the same substance.

Isomorphous substances have often very close points of resemblance, quite independently of form. Thus, arsenic and phosphorus have nearly the same odour, they both form gaseous compounds with hydrogen, they differ from nearly all other bodies in their mode of combining with oxygen, and yet agree with one another, and their salts are disposed to combine with the same quantity of water of crystallization. A similar analogy subsists between selenium and sulphur, both being fusible, volatile, and combustible in nearly the same degree, forming with hydrogen colourless gases which are similar in odour and in their chemical relations, and giving rise to analogous compounds with oxygen. The characters of sulphuric and selenic acids in particular are very similar; and the salts of these acids are equally allied. Sulphate of soda, for example, has the unusual property of being less soluble in water at 212° than at 100°, and the very same peculiarity is observable in seleniate of soda. The same intimacy of relation exists between chlorine, bromine, and iodine, between baryta and strontia, between lime and magnesia, and between cobalt and nickel, besides other cases, too numerous to mention here.

Isomorphous substances, owing doubtless to the various points of resemblance which have just been traced, crystallize together with great readiness, and are separated from each other with difficulty. Daubeny has remarked that a weak solution of lime, which in pure water would be instantly indicated by oxalate of ammonia, is very sluggishly affected by that test when much sulphate of magnesia is present; and I find that chloride of manganese cannot be purified from lime by oxalate of ammonia. A mixture of the sulphates of the protoxides of copper and iron yields crystals which have the same quantity of water of crystallization (6 equivalents), and the same form, as green vitriol, though they may contain a large quantity of copper. The sulphates of the protoxides of zinc and copper, of copper and magnesium, of copper and nickel, of zinc and manganese, and of magnesium and manganese, crystallize together, contain 6 equivalents of water, and have the same form as green vitriol, without containing a particle of iron. These mixed salts may be crystallized over and over again without the ingredients being separated from each other, just as it is extremely difficult to purify alum from peroxide of iron, with which alumina is isomorphous. In these instances the isomorphous salts do not occur in definite proportions; they are not chemically united as double salts, but merely crystallize together.

The same intermixture of isomorphous substances which takes place in artificial salts is found to occur in minerals, and affords a luminous explanation of the great variety both in the kind and proportion of substances which may coexist in a mineral species, without its external character being thereby essentially affected. Thus, garnet is a double silicate of alumina and lime, expressed by the formula $(Al_2O_3 + SiO_3) + 3(CaO + SiO_3)$; but in garnet, as in alum, the alumina may be replaced by peroxide of iron, yielding the compound $(Fe_2O_3 + SiO_3) + 3(CaO + SiO_3)$, or they may be both present in any proportion, provided that their sum is equivalent to either singly. So, while peroxide of iron displaces the alumina, the lime may be exchanged for protoxide of iron; and a mineral would result $(Fe_2O_3 + SiO_3) + (3FeO + SiO_3)$, which contains neither alumina nor lime, though it has still the form of garnet. Instead of protoxide of iron, the lime may be replaced by magnesia, protoxide of manganese, or any other isomorphous base; or any equivalent quantity of some or all of these may take the place of the lime, without the crystallographic character being destroyed. In like manner epidote is a double silicate of alumina and lime, expressed by $(Al_2O_3 + SiO_3) + (CaO + SiO_3)$; and here again varieties of epidote are to be expected, in which alumina and lime are replaced partially or wholly by an equivalent quantity of isomorphous bases.

The discovery of Mitscherlich, while it accounts for difference of composition in the same mineral, and serves as a caution to mineralogists against too exclusive reliance on crystallographic character, is in several other respects of deep interest to the chemist. It tends to lay open new paths of research by unfolding analogies which would not otherwise have been perceived.—The tendency of isomorphous bodies to crystallize together accounts for the difficulty of purifying mixtures of isomorphous salts by crystallization.—The same property sets the chemist on his guard against the occurrence of isomorphous substances in crystallized minerals. The native phosphates, for example, frequently contain arsenic acid, and conversely the native arseniates phosphoric acid, without the form of the crystals being thereby affected in the slightest degree.—It is a useful guide in discovering the atomic constitution of compounds. All chemists are agreed, from the composition of the oxides of iron, and from the compounds which this metal forms with other bodies, that the peroxide consists of two atoms of iron and three atoms of oxygen; and therefore it is inferred that alumina, which is isomorphous with peroxide of iron, has a similar constitution. The green oxide and acid of chromium, the oxygen of which is as 1 to 2, afford a still better illustration. As the chromates and sulphates are isomorphous, it was inferred that chromic, like sulphuric, acid was composed of one atom of the combustible to three atoms of oxygen. On this presumption it follows that the green oxide, containing half as much oxygen as the acid, must contain two atoms of chromium to three atoms of oxygen; and agreeably to this inference it is found that the green oxide is isomorphous with alumina and peroxide of iron, both in its uncombined state and in its compounds.—The phenomena presented by isomorphous bodies afford a powerful argument in favour of the atomic theory. The only mode of satisfactorily accounting for the striking identity of crystalline form observable, first, between two substances, and, secondly, between all their compounds which have an exactly similar composition, is by supposing them to consist of ultimate particles possessed of the same figure, and arranged in precisely the same order. Hence it appears, that in accounting for the connexion between form and composition, it is necessary to employ the very same theory, by which alone the laws of chemical union in definite proportions can be adequately explained.

It has been objected to some of the facts adduced in favour of isomorphism, that the forms of substances considered isomorphous are sometimes *approximate* rather than *identical.* The primary form of sulphate of strontia is a rhombic prism very similar to that of sulphate of baryta; but on measuring the inclination of corresponding sides in each prism, the difference is found to exceed two degrees; and similar differences are observable in the rhombohedron of the carbonates of lime and protoxide of iron. This has induced Professor Miller of Cambridge to indicate this *approximation* by the term *plesiomorphism* (πλησιος, near); and it has been brought forward in a clever essay by Brooke, as an argument against the whole doctrine of isomorphism, an essay which has received an able reply from the pen of Whewell. (Phil. Mag. and An., N. S., x. 161 and 401.)

Dimorphism.—In one of the essays above referred to, Mitscherlich observed that biphosphate of soda is capable of yielding two distinct kinds of crystals, which, though different in form, in composition appear to be identical. The more uncommon of the two forms resembled binarseniate of soda; but the more usual form is quite dissimilar. He subsequently discovered that sulphur is capable of yielding two distinct kinds of crystals; and the same phenomenon, now termed dimorphism, has been since observed in carbon, copper, suboxide of copper, protoxide of lead, titanic acid, subsulphuret of copper, bisulphuret of iron, biniodide of mercury, sal-ammoniac, chromate of lead, sulphates of nickel and zinc, with 7 eq. of water, and other salts of that class. The crystals of carbonate of lime in calcareous spar and in arragonite belong to different systems of crystallization, the former being rhombohedral, and the latter derived from a rhombic prism. Nitrate of potassa exhibits the same two forms as carbonate of lime, and vesuvian and garnet are the same compound in two distinct crystalline forms. Arsenious acid, and probably metallic arsenic also, affords an instance of the same kind. It would thus seem that elementary and compound bodies are capable of assuming two distinct crystalline forms. In the case of biphosphate of soda an explanation may be derived from the experiments of Graham on metaphosphoric acid ; but the fact, that an elementary substance is susceptible of assuming different forms, is very remarkable, and not fully explained. In another part of this work the existence of allotropic modifications of elementary bodies, such as sulphur, phosphorus, and carbon, has been pointed out ; and it is probable that each allotropic modification has a form peculiar to itself. We may also suppose, that when uniting with other bodies, these elements may retain, in the compounds, the peculiar allotropic state which they had at the moment of combination, and thus modify the form of the compound. This would account for the fact that the dimorphism of many compounds appears to depend on a difference in temperature or some other circumstances accompanying the formation of the compound.

In some cases *trimorphism* has been observed. Thus, rutile, brookite, and anatase are three distinct forms of titanic acid ; and other instances have been noticed.

Mitscherlich has also noticed that the form of salts is sometimes changed by heat, without their losing the solid state. This change was first noticed in sulphate of magnesia, and also in the sulphates of the protoxides of zinc and iron. It appears, in these instances at least, to be owing to decomposition of the hydrous salt effected by increased temperature ; a change of composition which is accompanied with a new arrangement in the molecules of the compound.

SECTION I.

CLASS OF SALTS, ORDER I.

OXY-SALTS.

This order of salts includes no compound the acid or base of which does not contain oxygen. With the apparent exception of the ammoniacal salts, both the acid and base of the salts described in this section are oxidized bodies. As each acid, with few exceptions, is capable of uniting with every alkaline base, and frequently in two or more proportions, it is manifest that the salts must constitute a very numerous class of bodies. It is necessary on this account to facilitate the study of them as much as possible by classification. They may be conveniently arranged by placing together those salts which contain either the same salifiable base or the same acid. It is not very material which principle of arrangement is adopted; but I give the preference to the latter, because, in describing the individual oxides, I have already mentioned the characteristic features of their salts, and have thus anticipated the chief advantage that arises from the former mode of classification. I shall therefore divide the salts into families, placing together those saline combinations which consist of the same acid united with different salifiable bases. The salts of each family, in consequence of containing the same acid, possess certain characters in common by which they may all be distinguished; and, indeed, the description of many salts, to which no particular interest is attached, is sufficiently comprehended in that of its family, and may therefore be omitted.

All the powerful alkaline bases, excepting ammonia, are the protoxides of an electro-positive metal, such as potassium, barium, or iron; so that if M represent an eq. of any one of those metals, $M + O$ or MO is the strongest alkaline base, and often the only one, which that metal can form. A single eq. of a monobasic acid neutralizes MO, forming with it a neutral salt. Thus, indicating an equivalent of sulphuric and nitric acid by the signs SO_3 and NO_5, all the neutral sulphates and nitrates of protoxides are indicated by $MO + SO_3$ and $MO + NO_5$. There is, therefore, in the neutral protosalts of each family, a constant ratio in the oxygen of the base and acid, resulting from the composition of each acid, that ratio for the sulphates being as 1 to 3, and for nitrates as 1 to 5. If the metal M of a neutral sulphate pass into a higher grade of oxidation, becoming a binoxide, MO_2, then will that binoxide be disposed to unite with 2 eq. of acid, and form a bisalt, $MO_2 + 2SO_3$, in which the oxygen of base and acid is still as 1 to 3; and if the metal yield a sesquioxide, M_2O_3, or a teroxide, MO_3, then, if sufficient acid be supplied, the resulting salts will consist of $M_2O_3 + 3SO_3$, and $MO_3 + 3SO_3$, the ratio of 1 to 3 being preserved. This curious law relative to oxy-salts, which is very general, was first noticed by Gay-Lussac (Mémoires d'Arcueil, ii.); and Berzelius has found it to hold in earthy minerals, and employed it as a guide in studying their composition.

The combination of salts with one another gives rise to compounds which were formerly called *triple* salts; but as the term *double* salt, proposed by Berzelius, gives a more correct idea of their nature and constitution, it will always be employed by preference. These salts may be composed of one acid and two bases, of two acids and one base, and of two different acids and two different bases. Most of the double salts hitherto examined consist of the same acid and two different bases.

The difference in the constitution of ammonia and that of all other bases capable of uniting with ox-acids, gives great interest to its salts. In another place, the probable existence of a compound radical formed of 1 eq. of nitrogen and 4 of hydrogen, and called by Berzelius ammonium, was pointed out. The oxide of this radical, which has not yet been obtained in an uncombined state, he considers as the basis of the oxy-salts of ammonia. This view is not supported by analogy alone, but is based on the remarkable fact, that in all the neutral salts of ammonia the quantity of water necessary to convert the ammonia into oxide of ammonium is always present, nor can it be removed without the total decomposition of the salt. H. Rose has indeed succeeded in obtaining anhydrous compounds of ammonia with the ox-acids; but he has at the same time shewn that they cannot be considered as salts, for although containing the elements for forming an anhydrous and neutral salt of ammonia, and produced by direct combination, neither the acid nor the alkali is present in the compound. This he has proved particularly in the substance formed by the union of anhydrous sulphuric acid with ammonia. (An. de Ch. et Ph. lxii. 389.) Strong evidence in its favour is likewise obtained from the views of isomorphism. It has been proved by Mitscherlich that in most of the crystallized salts of potassa, whether simple or double, the potassa may be replaced either partially or completely by an equivalent quantity of protohydrate of ammonia without any change in the form of the crystal. Ammonia with an eq. of water is therefore isomorphous with potassa, and as potassa is oxide of potassium, KO, so ammonia + 1 eq. water, $NH_3 + HO$, may be viewed as oxide of ammonium, NH_4,O; or if we represent ammonium, NH_4, by Am, then the oxide will be AmO; Am being a compound metal, and K, so far as we know, a simple one. The isomorphism of potassa and oxide of ammonium would naturally result from their analogy in constitution, since it is quite consistent with what we know concerning compound radicals, that the oxide of a compound metal should be isomorphous with that of a simple metal. There is one fact not easily explained, namely, that, while NH_4,O or AmO, replaces potassa, KO, without change of form in many salts, especially in alum and other double sulphates, sulphate of ammonia has the same form with sulphate of potassa only when it contains 1 eq. of water more; thus, AmO,HO,SO_3 is isomorphous with KO,SO_3. This would make KO in some compounds isomorphous with AmO, and in others with AmO, HO. The explanation of this anomaly is probably to be found in dimorphism. But that the oxide of a compound radical should be isomorphous with the oxide of a simple metal, is consistent with—nay, might be expected from, their known analogies.

Another view of the constitution of the oxy-salts of ammonia has recently been proposed by Graham. He supposes ammonia not to be a base, but to be one of a class of bodies which he calls basic adjuncts; a term used to denote a substance which, without being a base, is capable of entering into the constitution of a salt by attaching itself to other bases. Thus, the oxy-salts of ammonia he conceives to be salts of water, to the base of which ammonia is added as an adjunct. It is scarcely necessary to remark, that this view is not only inconsistent with the theory of isomorphism, but that the existence of adjunct bases is hypothetical, and arises from an endeavour to support another hypothesis, that all salts are neutral in composition.

SULPHATES.

The salts of sulphuric acid in solution may be detected by chloride of barium. A white precipitate, sulphate of baryta, invariably subsides, which is insoluble in acids and alkalies; a character by which the presence of sulphuric acid, whether free or combined, may always be recognized. An insoluble sulphate, such as sulphate of baryta or strontia, may be detected by mixing it, in fine powder, with three times its weight of carbonate of potassa or soda, and exposing the mixture in a platinum crucible for half an hour to a red heat. Double decomposition ensues; and on digesting the residue in water, filtering the solution, neutralizing the free alkali by pure hydrochloric, nitric, or acetic acid, and adding chloride of barium, the insoluble sulphate of that base is precipitated.

Several sulphates exist in nature, but the only ones which are abundant are the sulphates of lime and baryta. All of them may be formed by the action of sulphuric acid on the metals themselves, on the metallic oxides or their carbonates, or by way of double decomposition.

The solubility of the sulphates is very variable. There are six only which may be regarded as really insoluble; namely, the sulphate of baryta, and of the oxides of tin, antimony, bismuth, lead, and mercury. The sparingly soluble sulphates are those of strontia, lime, zirconia, yttria, and oxide of silver. All the others are soluble in water.

All the sulphates, those of potassa, soda, lithia, baryta, strontia, and lime excepted, are decomposed by a white heat. One part of the sulphuric acid of the decomposed sulphate escapes unchanged, and another portion is resolved into sulphurous acid and oxygen. Those which are easily decomposed by heat, such as sulphate of oxide of iron, yield the largest quantity of undecomposed sulphuric acid.

When a sulphate mixed with carbonaceous matter is ignited, the oxygen both of the acid and of the oxide unites with carbon, carbonic acid is disengaged, and a metallic sulphuret remains. A similar change is produced by hydrogen gas at a red heat, with formation of water, and frequently of some hydrosulphuric acid. In some instances the hydrogen entirely deprives the metal of its sulphur.

The composition of neutral protosulphates is expressed, as above stated, by the formula $MO + SO_3$. Consequently the acid contains three times as much oxygen as the base; and if both were deprived of their oxygen, a metallic protosulphuret would result, as indicated by the formula $M + S$.

In accordance with the views of Graham already given, the sulphates may be divided into three classes:—the first consisting of the anhydrous sulphates, being such as can exist without the eq. of constitutional water; the second, those in which the constitutional water forms an essential part; and the third composed of the double salts, which he considers as produced from the second by the eq. of constitutional water being replaced by an eq. of a sulphate of the first class. If dilute sulphuric acid be exposed in an open dish to a temperature not exceeding 380°, the evaporation proceeds without the slightest loss of acid until the sp. gr. is raised to 1·78, when it ceases entirely, and there remains a definite compound of 1 eq. of sulphuric acid and 2 eq. of water. One of these he considers as basic, the other as constitutional water, the acid of the mentioned strength being a salt, the constitution of which is represented by the formula HO,SO_3,HO. From it any one of the three classes of sulphates may be formed, the eq. of basic water being readily replaced by any stronger base, while the eq. of constitutional water can only be removed by a neutral salt producing the double salts, among which the bisulphates must also be included. There are, however, exceptions to the last observation, as Graham has remarked that magnesia and its class of isomorphous oxides are capable of acting the part of constitutional water. Although it would be highly advantageous to treat of the sulphates under the three classes above mentioned, it cannot yet be attempted; for although the constitutional water of several of them has been determined by Graham in his valuable essay already quoted, many of them have not yet been examined in reference to this point. The following table represents the constitution of the more important, both in their amorphous and crystallized state:—

Names.	Base.	Acid.	Equiv.	Formulæ.
Sulphate of Potassa . .	47·15 1 eq.+	40·1 1 eq. =	87·25	$KO+SO_3$.
Sesquisulph. do. . .	94·3 2 eq.+	120·3 3 eq. =	214·6	$2KO+3SO_3$.
Do. in crystals with	9 or 1 eq. of water . .		= 223·6	
Bisulph. Potassa . .	47·15 1 eq.+	80·2 2 eq. =	127·35	$KO+2SO_3$.
Do. with 9 or 1 eq. of water	. . . . . .		= 106·35	

Names.	Base.	Acid.	Equiv.	Formulæ.
Sulphate of Soda . .	31·3 1 eq.	+ 40·1 1 eq.	= 71·4	$NaO+SO_3$.
Do. in crystals with	90 or	10 eq. of water . .	=161·4	
Bisulph. Soda . . .	31·3 1 eq.	+ 80·2 2 eq.	=111·5	$NaO+2SO_3$.
Do. in crystals with	36 or	4 eq. of water . .	=147·5	
Sulphate of Lithia . .	18 1 eq.	+ 40·1 1 eq.	= 58·1	$LO+SO_3$.
Do. in crystals with	9 or	1 eq. of water . .	= 67·1	
Sulph. of ox. of Ammonium	26·15 1 eq.	+ 40·1 1 eq.	= 66·25	NH_4O+SO_3.
Do. in crystals with	9 or	1 eq. of water . .	= 75·25	
Sulphate of Baryta . .	76·7 1 eq.	+ 40·1 1 eq.	=116·8	$BaO+SO_3$.
Do. Strontia . .	51·8 1 eq.	+ 40·1 1 eq.	= 91·9	$SrO+SO_3$.
Do. Lime . .	28·5 1 eq.	+ 40·1 1 eq.	= 68·6	$CaO+SO_3$.
Do. as Gypsum with	18 or	2 eq. of water . .	= 86·6	
Sulphate of Magnesia .	20·7 1 eq.	+ 40·1 1 eq.		
		+9 aq. 1 eq. .	= 69·8	$MgO+SO_3HO$.
Do. in crystals with	54 or	6 eq. of water . .	=123·8	
Sulphate of Alumina .	51·4 1 eq.	+ 40·1 1 eq.	= 91·5	$Al_2O_3+SO_3$.
Do. in crystals with	81 or	9 eq. of water . .	=172·5	
Tersulph. Alumina . .	51·4 1 eq.	+120·3 3 eq.	=171·7	$Al_2O_3+3SO_3$.
Do. in crystals with	162 or	18 eq. of water . .	=333·7	
Sulph. protox. Manganese	35·7 1 eq.	+ 40·1 1 eq.		
		+9 aq. 1 eq. .	= 84·8	$MnO+SO_3HO$.
Do. in crystals with	36 or	4 eq. of water . .	=120·8	
Sulph. protox. Iron . .	36 1 eq.	+ 40·1 1 eq.		
		+9 aq. 1 eq. .	= 85·1	$FeO+SO_3HO$.
Do. in crystals with	45 or	5 eq. of water . .	=130·1	
Tersulph. perox. Iron .	80 1 eq.	+120·3 3 eq.	=210·3	$Fe_2O_3+3SO_3$.
Disulph. do. . .	160 2 eq.	+ 40·1 1 eq.	=200·1	$2Fe_2O_3+SO_3$.
Do. as a hydrate with	54 or	6 eq. of water . .	=254·1	
Sulph. protox. Zinc . .	40·3 1 eq.	+ 40·1 1 eq.		
		+9 aq. 1 eq. .	= 89·4	$ZnO+SO_3HO$.
Do. in crystals with	54 or	6 eq. of water . .	=143·4	
Sulph. protox. Nickel . .	37·5 1 eq.	+ 40·1 1 eq.		
		+9 aq. 1 eq. .	= 86·6	$NiO+SO_3HO$.
Do. in crystals with	54 or	6 eq. of water . .	=140·6	
Sulph. protox. Cobalt .	37·5 1 eq.	+ 40·1 1 eq.		
		+9 aq. 1 eq. .	=86·6	$CoO+SO_3HO$.
Do. in crystals with	49 or	5 eq. of water . .	=131·6	
Tersulph. ox. Chromium .	80 1 eq.	+120·3 3 eq.	=200·3	$Cr_2O_3+3SO_3$.
Sulph. protox. Copper .	39·6 1 eq.	+ 40·1 1 eq.		
		+9 aq. 1 eq. .	= 88·7	$CuO+SO_3HO$.
Do. in crystals with	36 or	4 eq. of water . .	=124·7	
Disulphate do. . .	79·2 2 eq.	+ 40·1 1 eq.	=119·3	$2CuO+SO_3$.
Sulph. protox. Mercury .	210 1 eq.	+ 40·1 1 eq.	=250·1	$HgO+SO_3$.
Subsulp. perox. do. . .	872 4 eq.	+120·3 3 eq.	=992·3	$4HgO_2+3SO_3$.
Bisulp. do. . .	218 1 eq.	+ 80·2 2 eq.	=298·2	HgO_2+2SO_3.
Sulph. ox. Silver . .	116 1 eq.	+ 40·1 1 eq.	=156·1	$AgO+SO_3$.

DOUBLE SULPHATES.

Sulphate of Soda and Lime	Sulphate of Soda	71·4	1 eq.	=140·0	NaO,SO_3+CaO,SO_3.
	do. Lime	68·6	1 eq.		
Sulph. of Potassa and Magnesia	Sulph. Patassa	87·25	1 eq.	=148·05	KO,SO_3+MgO,SO_3.
	do. Magnesia	60·8	1 eq.		
Do.	with 54 or 6 eq. of water . . .			=202·05	
Sulph. ox. of Ammonium & Mag.	Sulph. ox. Ammonium	57·25	1 eq.	=127·05.	NH_4O,SO_3+MgO,SO_3.
	do. Magnesia	60·8	1 eq.		
Do.	with 54 or 6 eq. of water . . .			=181·05	
Sulph. of Soda and Magnesia	Sulph. Soda	71·4	1 eq.	=132·2	NaO,SO_3+MgO,SO_3.
	do. Magnesia	60·8	1 eq.		
Do.	with 54 or 6 eq. of water . . .			=186·2	
Sulph. of Potassa and Alumina	Sulph. Potassa	87·25	1 eq.	=258·95	$KO,SO_3+Al_2O_33SO_3$.
	Tersulph. Alumina	171·7	1 eq.		
Do.	with 216 or 24 eq. of water . . .			=474·95	

Names.		Acid.		Equiv.	Formulæ.
Sulph. of Soda and Alumina	Sulph. Soda	71·4	1 eq.	=243·1	$NaO,SO_3+Al_2O_3,3SO_3$.
	Tersulph. Alumina	171·7	1 eq.		
Do.	with 234 or 26 eq. of water	. . .		=477·1	
Sulph. ox. Am. and Alumina	Sulph. ox. Ammonium	57·25	1 eq.	=228·95	$NH_4O,SO_3+Al_2O_3,3SO_3$.
	Tersulph. Alumina	171·7	1 eq.		
Do.	with 216 or 24 eq. of water	. . .		=444·95	
Sulph. Potassa & protox. Mang.	Sulph. Potassa	87·25	1 eq.	=163·05	KO,SO_3+MnO,SO_3.
	do. ox. Mangan.	75·8	1 eq.		
Do.	with 54 or 6 eq. of water	. . .		=217·05	
Sulph. ox. Am. and protox. Mang.	Sulph. Ammonium	57·25	1 eq.	=133·05	NH_4O,SO_3+MnO,SO_3.
	do. ox. Mang.	75·8	1 eq.		
Do.	with 54 or 6 eq. of water	. . .		=196·05	

The protoxides of iron, zinc, copper, nickel, and cobalt yield with potassa and ammonia double salts exactly agreeing in form and composition with the preceding double salts of magnesia and oxide of manganese.

Sulphate of Potassa.—This salt is easily prepared artificially by neutralizing carbonate of potassa with sulphuric acid; and it is procured abundantly by neutralizing with carbonate of potassa the residue of the operation for preparing nitric acid. Its taste is saline and bitter. It crystallizes in forms belonging to the right prismatic system, and its general form closely resembles the regular hexagonal prism, terminated by pyramids with six sides, the size of which is said to be much increased by the presence of a little carbonate of potassa. According to Mitscherlich it is isomorphous with chromate and seleniate of potassa, the constitution of which is analogous. (Pog. Annalen, xviii. 168.) The crystals contain no water of crystallization, and suffer no change by exposure to the air. They decrepitate when heated, and enter into fusion at a red heat. They require 16 times their weight of water at 60°, and five of boiling water for solution.

Bisulphate of potassa is easily formed by exposing the neutral sulphate with half its weight of strong sulphuric acid to a heat just below redness, in a platinum crucible, until acid fumes cease to escape. It is obtained in crystals from a concentrated solution at high temperatures, as in the cold the neutral sulphate is formed. The form is a right rhombic prism, which is in general so flattened as to be tabular. According to Graham they contain 1 eq. of water, which he considers to be basic; the bisulphate being a double sulphate of water and potassa. The anhydrous bisulphate has been prepared by Rose. It has a strong sour taste, and reddens litmus paper. It is much more soluble than the neutral sulphate, requiring for solution only twice its weight of water at 60°, and less than an equal weight at 212° F. It is resolved by heat into sulphuric acid and the neutral sulphate.

Phillips has described a sesquisulphate, obtained in the form of acicular crystals like asbestos, from the residue of the process for making nitric acid. The conditions for insuring its production have not been determined. (Phil. Mag. and Annals, ii. 421.)

Sulphate of Soda.—This compound, commonly called *Glauber's salt*, is occasionally met with on the surface of the earth, and is frequently contained in mineral springs. It may be made by the direct action of sulphuric acid on carbonate of soda ; and it is procured in large quantity as a residue in the processes for forming hydrochloric acid and chlorine.

Sulphate of soda has a cooling, saline, and bitter taste. It commonly yields forms belonging to the right prismatic system, and containing 10 eq. of water of crystallization, the whole of which is rapidly lost by efflorescence on exposure to the air. When heated they readily undergo the watery fusion. At 32°, 100 parts of water dissolve 12 parts of the crystals, 48 parts at 64·5°, 100 parts at 77°, 270 at 89·5°, and 322 at 91·5°. On increasing the heat beyond this point, a portion of the salt is deposited, being less soluble at higher temperatures than at 91·5°. (Gay-Lussac.) If a solution saturated at 91·5° is evaporated at a higher temperature, the salt is deposited in opaque anhydrous prisms, unconnected with, but of the same system as, the hydrous crystals. Its sp. gr. in this state is 2·462. (Haidinger.)

Bisulphate of soda may be formed in the same manner as the analogous salt of potassa.

Sulphate of Lithia.—This salt is very soluble in water, fuses by heat more readily than the sulphates of the other alkalies, and crystallizes in flat prisms, which resemble sulphate of soda in appearance, but do not effloresce on exposure to the air. Its taste is saline without being bitter.

Sulphate of Oxide of Ammonium.—This salt is easily prepared by neutralizing carbonate of ox. of ammonium with dilute sulphuric acid ; and it is contained in considerable quantity in the soot from coal. It crystallizes in long flattened six-sided prisms. It dissolves in two parts of water at 60°, and in an equal weight of boiling water. In a warm dry air it effloresces and loses 1 eq. of water. When sharply heated, it fuses, and is decomposed, yielding nitrogen gas, water, and sulphate of ox. of ammonium. It has been already mentioned, that although the salt NH_4O,SO_3, or AmO,SO_2, the anhydrous sulphate of oxide of ammonium, replaces anhydrous sulphate of potash, KO,SO_3, in the alums and other double sulphates, yet the sulphate of oxide of ammonium does not assume the same form as sulphate of potassa, unless it contains an additional eq. of water ; so that KO,SO_3 is isomorphous with $AmO,SO_3 + HO$. This anomaly probably depends on dimorphism in some of the elements.

The anhydrous compound was formed by Rose by conducting dry ammoniacal gas into a glass vessel coated by a thin film of perfectly anhydrous sulphuric acid. When no excess of acid is present, it undergoes no change in the air, and is soluble without change in water, from which it crystallizes irregularly, but in forms different from those of the common sulphate. It is remarkable that the sulphuric acid is only partially precipitated by chloride of barium in the cold, and no precipitate whatever is produced by chlorides of strontium or lime until heat is applied, and even then the action is imperfect. Nor, on the other hand, can the ammonia be separated by the chloride of platinum. From this it follows that neither the sulphuric acid nor the ammonia can be present in the solution, although their elements are present in equivalent proportions. It is not improbable it may be an amide, and formed of $NH_2SO_2 + HO$.

Sulphate of Baryta.—Native sulphate of baryta, commonly called *heavy spar*, occurs abundantly, chiefly massive, sometimes forming even mountain masses, as, for example, in Ayrshire, where a hill composed of this mineral is said to exist; but often in anhydrous crystals, the form of which is variable, being sometimes prismatic and sometimes tabular, deducible from a right rhombic prism. Its density is about 4·4. It is easily formed artificially by double decomposition. This salt bears an intense heat without fusing or undergoing any other change, and is one of the most insoluble substances with which chemists are acquainted. It is sparingly dissolved by hot and concentrated sulphuric acid, but is precipitated by the addition of water. When mixed, in fine powder, with $\frac{1}{6}$th of its weight of lamp-black, and ignited in a closed crucible, it is deoxidized, yielding sulphuret of barium, a compound much used in chemistry, both as such, and as affording a ready means of obtaining baryta and the other compounds of barium. If the ignition with charcoal has not been continued long enough, the acid, and part only of the base of the salt, are deoxidized, and the mass boiled in water yields an orange-coloured solution, which on cooling deposits hydrate of baryta, while persulphuret of barium remains in solution. Assuming the persulphuret here formed to be a bisulphuret, the following equation explains the change:—$2(BaO,SO_3) + C_7 = BaO + BaS_2 + 7CO$. If the persulphuret be a quintosulphuret, the equation will be as follows:—$5(BaO,SO_3) + C_{16} = 4BaO + BaS_5 + 16CO$. From the very large proportion of hydrate of baryta which I have usually obtained in this process, I suspect the latter to be the true explanation.

Sulphate of Strontia.—This salt, the *celestine* of mineralogists, is less abundant than heavy spar. It occurs in anhydrous prismatic crystals of peculiar beauty in Sicily, and is isomorphous with the sulphate of baryta. It is also found in considerable quantity in Derbyshire, in masses formed of small irregular crystals. Its density is 3·858. As obtained by the way of double decomposition, it is a white heavy powder, very similar to sulphate of baryta, and requires about 3840 times its weight of boiling water for solution. When ignited with charcoal it yields the same results as the preceding salt.

Sulphate of Lime.—This salt is easily formed by mixing in solution a salt of lime with any soluble sulphate. It occurs abundantly as a natural production. The mineral called *anhydrite* is anhydrous sulphate of lime; and all the varieties of *gypsum* are composed of the same salts, united with water. The pure crystallized specimens of gypsum are sometimes called *selenite;* and the white compact variety is employed in statuary under the name of *alabaster.* The crystals of anhydrite belong to the right prismatic system, and are isomorphous with the sulphates of baryta and strontia, while the forms of gypsum are oblique prismatic. The latter, which are by far the more general, are readily recognized by the perfect cleavage plane which truncates the acute angle of the prism. They contain 2 eq. of water, one only of which is considered by Graham to be water of crystallization, the other being constitutional. The former is readily lost by exposing pounded gypsum to a temperature of 212° *in vacuo*, and the whole water is expelled by a temperature below 300°. When dried by a heat not exceeding 260° or 270°, which expels the first eq. of water, it constitutes the well-known plaster of Paris, which, when mixed with a proper proportion of water, rapidly becomes dry and solid, owing to the reproduction of gypsum. But if heated beyond 270°, yet not so as to expel the second eq. of water, it loses the property of hardening when made into a paste with water, although still identical in composition with properly burned gypsum. It is said in this case to be burnt dead, or killed. A heat of from 320° to 400° expels the remaining eq. of water; and, in the latter case, the powder is a perfect anhydrite. (Phil. Mag. vi. 417.)

Sulphate of lime has hardly any taste. It is considerably more soluble than the sulphate of baryta or strontia, requiring for solution about 500 parts of cold, and 450 of boiling water. Owing to this circumstance, and to its existing so abundantly in the earth, it is frequently contained in spring-water, to which it communicates the property called hardness. When freshly precipitated it may be dissolved completely by dilute nitric acid. It is commonly believed to sustain a white heat without decomposition; but Thomson states that it parts with some of its acid when heated to redness.

Sulphate of Magnesia.—This sulphate, generally known by the name of *Epsom* salt, is frequently contained in mineral springs. It may be made directly, by neutralizing dilute sulphuric acid with carbonate of magnesia; but it is procured for the purposes of commerce by the action of dilute sulphuric acid on magnesian limestone, native carbonate of lime and magnesia.

Sulphate of magnesia has a saline, bitter, and nauseous taste. It crystallizes readily, under 125°, in small quadrangular prisms, which effloresce slightly in a dry air. It is obtained also in larger crystals, the principal form in which is a right rhombic prism, the angles of which are 90° 30′ and 89° 30′. (Brooke.) Its crystals are soluble in an equal weight of water at 60°, and in three-fourths of their weight of boiling water. They undergo the watery fusion when heated; and the anhydrous salt is deprived of a portion of its acid at a white heat. Dried at 212° it retains 2 eq. of water; but one of these is expelled at 270°, while the other is retained till the temperature rises to 460°. When the solution crystallizes at temperatures above 125°, it yields oblique rhombic prisms, being an instance of dimorphism. The crystals of the first form, when warmed beyond 125°, become opaque, and are then found to be an aggregate of minute crystals of the second form. We shall see the same phenomenon in the sulphates of zinc and nickel.

Sulphates of Alumina.—The tersulphate is prepared by saturating dilute sulphuric acid with hydrated alumina, and evaporating. It crystallizes with difficulty in thin flexible plates of a pearly lustre, which contain 18 eq. of water, and require twice their weight of water for solution. Its solution is much used in the arts as a mordant. Berzelius says it occurs native at Milo, in the Grecian Archipelago. It has an acid reaction.

The hydrated disulphate is known to mineralogists under the name of *aluminite*, which occurs at Halle, on the river Saal, and at Newhaven in Sussex; and Berzelius says the same compound falls when ammonia is added to a solution of the tersulphate. It is insoluble in water, and by heat is first rendered anhydrous, and then its acid is expelled, leaving pure alumina. The composition given in the table is from an analysis of aluminite from both its localities by Stromeyer.

Sulphate of Protoxide of Manganese.—This salt is best obtained by dissolving pure carbonate of manganese in moderately dilute sulphuric acid, and setting the solution aside to crystallize by spontaneous evaporation. The crystals are transparent, and of a slight rose tint, in taste resemble Glauber's salt, and belong to the doubly oblique prismatic system. It is insoluble in alcohol, but dissolves in twice and a half its weight of cold water. If the heat is gradually applied, it may be increased to redness without expelling any of the acid.

Sulphates of the Oxides of Iron.—Sulphate of the protoxide, commonly called *green vitriol*, is formed by the action of dilute sulphuric acid on metallic iron, or by exposing protosulphuret of iron in fragments to the combined agency of air and moisture. The salt has a strong styptic, inky taste. When perfectly pure it does not change vegetable blue colours, though generally stated to do so, the reddening effect being only produced when some of the iron passes into a higher state of oxidation, as has been shewn by Bonsdorff. (Pogg. An. xxxi. 81.) He finds that the oxidation, which occurs with extreme facility in a perfectly neutral solution, is completely prevented by a few drops of sulphuric acid in excess, and the resulting crystals have a distinctly blue colour. The common green tint is consequently a delicate test of the presence of peroxide of iron. The crystals belong to the oblique prismatic system, and contain 6 eq. of water, one of which is retained, according to Graham, till the temperature rises to 535°. By operating carefully it may be rendered anhydrous without the loss of acid. It is soluble in two parts of cold and in three-fourths of its weight of boiling water. This salt is employed in the manufacture of fuming sulphuric acid, in dyeing and calico-printing, and for the manufacture of ink. It is also much used in medicine.

The tersulphate of the peroxide is formed by mixing with a solution of the protosulphate exactly half as much sulphuric acid as that salt contains, and adding to the mixture in a boiling state successive portions of nitric acid until nitrous acid fumes cease to appear. The solution is then evaporated to dryness to expel the excess of nitric acid, and the tersulphate remains as a white salt. After being strongly heated, it dissolves slowly in water; but if evaporated at a gentle heat, it is deliquescent, and very soluble in water and alcohol, but insoluble in strong sulphuric acid. At a red heat it gives out all its acid, and peroxide of iron is left. Its solution in water has an orange colour, which is yellow when much diluted.

The disulphate of the peroxide falls as a hydrate of an ochreous colour, when a solution of the protosulphate is kept in an open vessel.

Sulphate of Oxide of Zinc.—This salt, frequently called *white vitriol*, is the residue of the process for forming hydrogen gas by the action of dilute sulphuric acid on metallic zinc; but it is also made, for the purposes of commerce, by roasting native sulphuret of zinc. It crystallizes by spontaneous evaporation in transparent flattened four-sided prisms of the right prismatic system, and isomorphous with Epsom salts; but at temperatures above 125° it forms oblique rhombic prisms, isomorphous with the third form of sulphate of nickel, and the second of sulphate of magnesia. The crystals dissolve in two parts and a half of cold, and are still more soluble in boiling water. The taste of this salt is strongly styptic. It reddens vegetable blue colours, though in composition it is a strictly neutral salt.

Sulphate of Protoxide of Nickel.—This salt, like the salts of nickel in general, is of a green colour, and crystallizes from its solution in pure water below 60°, in right rhombic prisms exactly similar to the sulphates of zinc and magnesia. Between 60° and 70° it forms acute quadratic octohedrons, and above 86° it crystallizes in oblique rhombic prisms. In all these forms the salt has the same composition, and exhibits, therefore, an instance of trimorphism. The crystals of the first form, when exposed to the light, become opaque and are converted into an aggregate of crystals of the second form. If an excess of sulphuric acid is present, the crystals are square prisms, which, according to R. Phillips and Cooper, contain rather less water and more acid than the preceding; though the difference is not so great as to indicate a different atomic constitution. (Annals of Philosophy, xxii. 439.) Thomson says he analyzed both kinds, and found their composition identical. It is soluble in about three times its weight of water at 60° F.

Sulphate of Protoxide of Cobalt.—When protoxide of cobalt is digested in dilute sulphuric acid, a red solution is formed, which by evaporation deposits crystals of the same colour. Mitscherlich has shewn that the crystals are identical in composition with sulphate of protoxide of iron; and Brooke's measurements prove these salts to be isomorphous. (An. of Phil., N. S., vi. 120.) They are insoluble in alcohol, and dissolve in about 24 parts of cold water.

Tersulphate of Oxide of Chromium.—This salt may be formed by saturating dilute sulphuric acid with hydrated oxide of chromium; but it has not been obtained in crystals.

Sulphates of the Oxides of Copper.—Sulphate of the red oxide of copper has not been obtained in a separate state. The sulphate of the black, or protoxide, *blue vitriol*, employed by surgeons as an escharotic and astringent, may be prepared by roasting the native sulphuret; but it is more generally made by directly dissolving the protoxide in dilute sulphuric acid, and crystallizing by evaporation. This salt forms crystals of a blue colour, reddens litmus paper, and is soluble in about four of cold, and in two parts of boiling water. The crystals contain 5 eq. of water, four of which are lost at 212° in a dry air, but the fifth is retained till the temperature exceeds 430°. It is then a white powder, which combines readily with water, with the development of considerable heat. It is isomorphous with sulphate of protoxide of manganese.

When pure potassa is added to a solution of the sulphate of protoxide of copper in a quantity insufficient for separating the whole of the acid, a pale blueish-green precipitate, the disulphate, is thrown down.

Sulphate of protoxide of copper and ammonia is generated by dropping pure ammonia into a solution of the sulphate, until the sub-salt at first thrown down is nearly all dissolved. It forms a dark blue solution, from which, when concentrated, crystals are deposited by the addition of alcohol. It may be formed also by rubbing briskly in a mortar two parts of crystallized sulphate of protoxide of copper with three parts of carbonate of ammonia, until the mixture acquires an uniform deep blue colour. Carbonic acid gas is disengaged with effervescence during the operation, and the mass becomes moist, owing to the water of the blue vitriol being set free.

This compound, which is the *ammoniuret of copper* of the Pharmacopœia, contains sulphuric acid, protoxide of copper, and ammonia; but its precise nature has not been determined in a satisfactory manner. It parts gradually with ammonia by exposure to the air. Its empirical formula is $CuO,2NH_3 + HO,SO_3$.

Sulphates of the Oxides of Mercury.—When two parts of mercury are gently heated in three parts of strong sulphuric acid, so as to cause slow effervescence, a sulphate of the protoxide of mercury is generated. But if a strong heat is employed in such a manner as to excite brisk effervescence, and the mixture is brought to dryness, a bisulphate of the peroxide results, both being anhydrous. (Donovan in An. of Phil. xiv.) When this bisulphate, which is the salt employed in making corrosive sublimate, is thrown into hot water, decomposition ensues, and a yellow sub-salt, formerly called *turpeth mineral*, subsides. This salt is said by Phillips to consist of 3 eq. of acid and 4 of the peroxide. The hot water retains some of the bisulphate in solution, together with free sulphuric acid.

Sulphate of Oxide of Silver.—As this salt is rather sparingly soluble in water, it may be formed by double decomposition from concentrated solutions of nitrate of oxide of silver and sulphate of soda. It may also be procured by dissolving silver in sulphuric acid which contains about a tenth part of nitric acid, or by boiling silver in an equal weight of concentrated sulphuric acid. It requires about 80 times its weight of hot water for solution, and the greater part is deposited in small needles on cooling. By slow evaporation from a solution containing a little nitric acid, Mitscherlich obtained it in the form of a rhombic octohedron, the angles of which are almost identical with that of anhydrous sulphate of soda. Seleniate of oxide of silver is isomorphous with the sulphate.

Sulphate of oxide of silver forms with ammonia a double salt, which crystallizes in rectangular prisms, the solid angles and lateral edges of which are commonly replaced by tangent planes. It consists of 1 eq. of oxide of silver, 1 of acid, and 2 of ammonia; and it is formed by dissolving sulphate of oxide of silver in a hot concentrated solution of ammonia, from which on cooling the crystals are deposited. This salt is isomorphous with a double chromate and seleniate of oxide of silver and ammonia, which have a similar constitution, and are formed in the same manner. (Mitscherlich in An. de Ch. et Ph. xxxviii. 62.)

DOUBLE SULPHATES.

Sulphates of Lime and Soda.—This compound, the glauberite of mineralogists, occurs in very flat oblique rhombic prisms. Berthier prepared it by fusing together sulphate of lime with sulphate of soda in the ratio of their equivalents. Sulphate of soda, fused in similar proportions with the sulphates of magnesia, baryta, and oxide of lead, gives analogous compounds. In these instances, however, the affinity is so feeble, that it is overcome by the mere action of water. (An. de Ch. et Ph. xxxviii. 255.)

Sulphate of Potassa and Magnesia.—On mixing solutions of these salts in atomic proportion, the double salt is formed either by spontaneous evaporation or on cooling from a hot rather concentrated solution. The crystals are prismatic and of a complicated form, belonging to the oblique prismatic system. (Brooke.) A similar double salt, isomorphous with the preceding, is formed by substituting ammonia for potassa. Their composition is given in the table.

Similar pairs of double salts may be formed with the protoxides of manganese, iron, zinc, copper, cobalt, and nickel. These salts have the same form and composition as the corresponding salt of magnesia.

Alum.—This well-known substance is a double sulphate of potassa and alumina, which crystallizes with great facility from a solution containing its elements. It is prepared in this country from alum-slate, an argillaceous slaty rock highly charged with pyrites: on roasting this rock, the sulphuret of iron is oxidized, the resulting sulphuric acid unites with alumina and potassa present in the slate, and the alum is dissolved out by water. By frequent crystallization it is purified from the oxide of iron, which obstinately adheres to it. In Italy it is prepared from *alum-stone*, which occurs at Tolfa near Rome, and in most volcanic districts, being formed apparently by the action of sulphurous acid vapours on felspathic rocks. The materials of the alum exist in the stone ready formed; and they are extracted by gently heating the rock, exposing it for a time to the air, and lixiviation. The alum from this source has long been prized, in consequence of being quite free from iron. In both of these processes the alkali contained in the alum-rock is inadequate for uniting with the sulphate of alumina which is obtained, and hence a salt of potassa must be added. A method has lately been proposed for obtaining alum from felspar, which is a compound of alumina, potassa, and silicic acid, the bases being in the proportion to form alum. The felspar is so decomposed as to substitute sulphuric acid for the silicic acid, when alum results.

Alum has a sweetish astringent taste, and reddens litmus paper. It is soluble in five parts of water at 60°, and in little more than its own weight of boiling water. It crystallizes readily in octohedrons, or in segments of the octohedron, and the crystals contain 24 eq. or almost 50 per cent. of water of crystallization. On being exposed to heat, they froth up remarkably, and part with all the water, forming anhydrous alum, the *alumen ustum* of the Pharmacopœia. At a full red heat the alumina is deprived of its acid.

Alum is employed in the formation of a spontaneously inflammable mixture long known under the name of *Homberg's pyrophorus.* It is made by mixing equal weights of alum and brown sugar, and stirring the mass over the fire in an iron or other convenient vessel till quite dry: it is then put into a glass tube or bottle, and heated to moderate redness without exposure to the air, until inflammable gas ceases to be evolved. A more convenient mixture is made with three parts of lamp-black, four of burned alum, and eight of carbonate of potassa. When the pyrophorus is well made, it speedily becomes hot on exposure to the air, takes fire, and burns like tinder; but the experiment frequently fails from the difficulty of regulating the temperature.

From the recent experiments by Gay-Lussac, it appears that the essential ingredient of Homberg's pyrophorus is sulphuret of potassium in a state of minute division. The charcoal and alumina act only by being mechanically interposed between its particles; but when the mass once kindles, the charcoal takes fire and continues the combustion. He finds that an excellent pyrophorus is made by mixing 27 parts of sulphate of potassa with 15 parts of calcined lamp-black, and heating the mixture to redness in a common hessian crucible, of course excluding the air at the same time. (An. de Ch. et Ph. xxxvii. 415.)

Alum, having exactly the same form, composition, appearance, and taste as the salt just described, may be made with ammonia, the sulphate of which replaces sulphate of potassa. It is met with occasionally as a natural product, and may be prepared by evaporating a solution of sulphate of ammonia with tersulphate of alumina.

A soda alum may also be prepared, similar in form and composition to the preceding alums, except that it contains 26 equivalents of water. (Berzelius.) This salt is disposed to effloresce in the air.

Iron Alum.—By mixing sulphate of potassa with tersulphate of peroxide of iron, and crystallizing by spontaneous evaporation, crystals are obtained similar to common alum in form, *colour*, *taste*, and composition. This salt has often a pink tint, but is sometimes quite colourless. A similar double salt, quite colourless, may be made with ammonia instead of potassa. In both these alums the alumina is simply replaced by an equivalent quantity of peroxide of iron.

Chrome Alums.—The tersulphate of oxide of chromium forms with the sulphates of potassa and ammonia double salts, which are exactly similar in form and composition to the preceding varieties of alum. They appear black by reflected, but purplish-red by transmitted light.

Manganese Alum.—Mitscherlich obtained this salt by mixing a solution of tersulphate of sesquioxide of manganese with sulphate of potassa, and evaporating to the consistence of syrup by a very gentle heat. On cooling, octohedral crystals of a brownish violet colour were deposited, which were similar in composition to common alum. The tersulphate used for the purpose is prepared by macerating sesquioxide of manganese in very fine powder with strong sulphuric acid: it is made with difficulty, owing to the indisposition of that oxide to unite with acids, and to its ready conversion by heat into sulphate of the protoxide.

From the descriptions of the salts to which the term alum has been applied, it will be observed that they are characterized by two common properties: they all crystallize in the octohedral system, and they are all constituted as represented by the formula $RO,SO_3 + R_2O_3.3SO_3 + 24$ aq., where RO represents an eq. of potassa, soda, or oxide of ammonium, and R_2O_3 any of the isomorphous oxides of aluminium, iron-manganese, and chromium. As Berzelius has ably remarked, the for, mula and crystalline form serve to determine the genus alum, and the oxidized bases its species.

Sulphate of Protoxide of Iron and Alumina.—This salt, which has recently been formed by Klauer, is obtained by the spontaneous evaporation of a mixture of sulphate of protoxide of iron and tersulphate of alumina in eq. proportions, a large excess of sulphuric acid being present. (Lieb. An. xiv. 261.) The salt is deposited in long acicular crystals, the constitution of which, being $FeO,SO_3 + Al_2O_3,3SO_3 + 24HO$, is similar to that of an alum; but as the crystals do not belong to the octohedral system, it has been improperly described as one of that class.

A compound, exactly analogous, in which protoxide of manganese is substituted for protoxide of iron, occurs native on the Gold Coast of Africa, in beautiful silvery fibres, many inches long. It has been described and analyzed by Apjohn, who found its formula to be $MnO, SO_3 + Al_2O_3,3SO_3 + 24HO$.

A similar salt of magnesia was obtained in the same manner; and it is exceedingly probable that a similar compound might be formed with the isomorphous oxides of zinc, copper, nickel, cobalt, and with lime. These, in their turn, might again be varied by substituting for the alumina the sesquioxides of iron, manganese, and chromium.

Anhydrous Sulphates with Ammonia.—Rose has observed that some sulphates possess the property of absorbing ammonia, and of forming with it definite compounds, which differ from sulphates of ammonia prepared in the moist way, both by containing no water of crystallization, and by the facility with which the alkali is again given out. They are formed by placing the anhydrous sulphate in a glass tube, and transmitting over it at common temperatures ammoniacal gas, well dried by fused potassa, as long as any increase of weight is observed: some sulphates absorb the gas very rapidly at first, and with disengagement of heat; but the absorption afterwards becomes slow, and requires a day or two in order to be complete. The salts most remarkable for this property are those which, in solution, are disposed to unite with ammonia.—Sulphate of protoxide of copper greedily absorbs ammonia, and acquires a deep blue colour similar to the ammoniuret of copper, prepared with moisture; but the former compound consists of 2 eq. of sulphate of protoxide of copper and 5 eq. of ammonia, while the latter contains 1 eq. of sulphate of copper, 2 of ammonia, and 1 eq. of water. Sulphate of protoxide of cobalt, as well as that of nickel, unites with 3 eq. of ammonia; that of zinc with 2·5, and that of manganese with 2 eq. The latter when heated loses all its ammonia, and returns to its original condition; whereas most of the other ammoniaco-sulphates suffer partial decomposition at the same time. Sulphate of oxide of silver unites with 1 eq. of ammonia; and a similar compound was prepared by C. G. Mitscherlich, but with 2 eq. of ammonia. With most of the other anhydrous sulphates ammonia refuses to unite.

On considering the nature of these compounds, one is at first disposed to associate them with double salts, supposing the acid to be divided between the two bases. But this opinion is rendered unlikely by the large quantity of combined ammonia, by the facility with which the alkali is given off, and by the absence of water, so constantly present in other ammoniacal sulphates. Rose, with much plausibility, compares these compounds to hydrates: water acts as a feeble base to saline compounds, combining with some in one or more proportions, and not at all with others, differing greatly in the ratio in which it combines with different salts, and being abandoned with great facility, often by mere exposure to the air. The same features characterise the combinations of ammonia with the anhydrous sulphates. (Pog. Annalen, xx. 149.)

The sulphates are not the only salts which absorb ammonia. Rose found that the nitrate of oxide of silver unites with 3 eq. of ammonia, and the gas, if freely supplied, is at first absorbed with such rapidity, and the corresponding increase of temperature is so great, that the salt enters into fusion. Heat expels the ammonia before the nitrate of oxide of silver is decomposed. A similar compound, but with less ammonia, was formed by C. Mitscherlich.

SULPHITES.

The salts of sulphurous acid have lately been minutely examined by Muspratt. The sulphites of potassa, soda, and ammonia, which are made by neutralizing those alkalies with sulphurous acid, are soluble in water; but most of the other sulphites, so far as is known, are of sparing solubility. The sulphites of baryta, strontia, and lime are very insoluble in water, but dissolve in an excess of the acid; and consequently the soluble salts of these earths decompose the alkaline sulphites.

The stronger acids, such as the sulphuric, hydrochloric, phosphoric, and arsenic acids, decompose all the sulphites with effervescence, owing to the escape of sulphurous acid, which may easily be recognized by its odour. Nitric acid, by yielding oxygen, converts the sulphites into sulphates.

When the sulphites of the fixed alkalies and alkaline earths are strongly heated in close vessels, the sulphate is generated, and a portion of sulphur sublimed. In open vessels at a high temperature they absorb oxygen, and are converted into sulphates; and a similar change takes place even in the cold, especially when they are in solution. Gay-Lussac has remarked, that a neutral sulphite always forms a neutral sulphate when its acid is oxidized; a fact from which it may be inferred that neutral sulphites consist of 1 eq. of the acid and 1 eq. of the base.

Muspratt has shewn that the sulphites, in general, are analogous in constitution to the carbonates. He has described several bisulphates, analogous to the bicarbonates.

The hyposulphates and hyposulphites are of such little practical importance, that it is unnecessary to describe individual salts; their general character has been already given. For a particular description of the hyposulphates, the reader is referred to an essay by Heeren. (An. de Chem. et Pharm. xl. 30.) The hyposulphite of soda alone is made on a large scale, and used in the Daugerreotype process, from its power of dissolving the compounds of silver.

NITRATES.

The nitrates may be prepared by the action of nitric acid on metals, and on the salifiable bases themselves, or on carbonates. As nitric acid forms soluble salts with all alkaline bases, the acid of the nitrates cannot be precipitated by any reagent. They are readily distinguished from other salts, however, by the characters already described.

All the nitrates are decomposed without exception by a high temperature; but the changes which ensue are modified by the nature of the oxide. Nitrate of oxide of palladium is decomposed at such a moderate temperature, that a great part of the acid passes off unchanged. Nitrate of oxide of lead requires a red heat, by which it is resolved, as already mentioned, into oxygen and nitrous acid. In some instances the changes are more complicated. With nitre, for example, nitrite of potassa is at first generated, with escape of oxygen gas: as the heat increases, the nitrous acid is resolved into binoxide of nitrogen and oxygen, the former of which remains in combination with potassa; the binoxide is then resolved into protoxide of nitrogen and oxygen, the former being retained by the alkali; and, lastly, nitrogen gas is disengaged, and peroxide of potassium remains. If the operation is performed in an earthen vessel, the peroxide will be more or less decomposed, in consequence of the affinity of the earthy substances for potassa. The preceding facts have been chiefly collected from the observations of Phillips and Berzelius. The tendency of potassa and soda to unite with protoxide of nitrogen was first discovered by Davy; and Hess has lately remarked that similar compounds are obtained with soda, baryta, and lime, as well as potassa, when their nitrates are heated until the disengaged gas is found to extinguish a light.

As the nitrates are easily decomposed by heat alone, they must necessarily suffer decomposition by the united agency of heat and combustible matter. The nitrates on this account are much employed as oxidizing agents, and frequently act with greater efficacy even than nitrohydrochloric acid. Thus metallic titanium, and the alloy of iridium and osmium, which resist the action of these acids, combine with oxygen when heated with nitre. The efficiency of this salt, which is the nitrate usually employed for the purpose, depends not only on the affinity of the combustible for oxygen, but likewise on that of the oxidized body for potassa. The process for oxidizing substances by means of nitre is called *deflagration*, and is generally performed by mixing the inflammable body with an equal weight of the nitrate, and projecting the mixture in small portions at a time into a red-hot crucible.

All the neutral nitrates of the fixed alkalies and alkaline earths, together with most of the neutral nitrates of the common metals, are composed of 1 eq. of nitric acid, and 1 eq. of a protoxide. Consequently, the oxygen of the oxide and acid in all such salts must be in the ratio of 1 to 5, the general formula being $MO + NO_5$.

The only nitrates found native are those of potassa, soda, lime, and magnesia.

The composition of the principal nitrates is exhibited in the following table :—

Names.	Base.	Acid.	Equiv.	Formulæ.
Nitrate of Potassa . .	47·15	1 eq.+54·15	1 eq.=101·3	$KO+NO_5$.
——— Soda . .	31·3	1 eq.+54·15	1 eq.= 85·45	$NaO+NO_5$.
Oxide of Ammonium .	17·15	1 eq.+54·15	1 eq.= 80·3	H_4NO+NO_5.
Nitrate of Baryta . .	76·7	1 eq.+54·15	1 eq.=130·85	$BaO+NO_5$.
——— Strontia . .	51·8	1 eq.+54·15	1 eq.=105·95	$SrO+NO_5$.
Do. in prisms with 45 or 5 eq. of water .			=150·95	
Nitrate of Lime . .	28·5	1 eq.+54·15	1 eq.= 82·65	$CaO+NO_5$.
——— Magnesia .	20·7	1 eq.+54·15	1 eq.= 74·85	$MgO+NO_5$.
——— Protox. Copper	39·6	1 eq.+54·15	1 eq.= 93·75	$CuO+NO_5$.
Do. in prisms with 63 or 7 eq. of water ? .			=156·75	
Nitrate of protox. Lead .	111·6	1 eq.+54·15	1 eq.=165·75	$PbO+NO_5$.
Dinitrate of ditto . .	223·2	2 eq.+54·15	1 eq.=277·35	$2PbO+NO_5$.
Nitrate of protox. Mercury	210	1 eq.+54·15	1 eq.=264·15	$HgO+NO_5$.
Do. in crystals with 18 or 2 eq. of water .			=282·15	
Nitrate of perox. Mercury	218	1 eq.+54·15	1 eq.=272·15	HgO_2+NO_5.
Dinitrate do.	436	2 eq.+54·15	1 eq.=490·15	$2HgO_2+NO_5$.
Nitrate of ox. Silver .	116	1 eq.+54·15	1 eq.=170·15	$AgO+NO_5$.

Nitrate of Potassa.—This salt is generated spontaneously in the soil, and crystallizes upon its surface, in several parts of the world, and especially in the East Indies, whence the greater part of the nitre used in Britain is derived. In some parts of the Continent, it is prepared artificially from a mixture of common mould or porous calcareous earth with animal and vegetable remains containing nitrogen. When a heap of these materials, preserved moist and in a shady situation, is moderately exposed to the air, nitric acid is gradually generated, and unites with the potassa, lime, and magnesia, which are commonly present in the mixture. On dissolving these salts in water, and precipitating the two earths by carbonate of potassa, a solution is formed, which yields crystals of nitre by evaporation. The nitric acid is by some supposed to be generated under these circumstances by the nitrogen of the organic matters combining directly, during putrefaction, with the oxygen of the atmosphere, a change which must be attributed to the affinity of oxygen for nitrogen, aided by that of nitric acid for alkaline bases. The nitre made in France is often said to be formed by this process; but the greater part is certainly obtained by lixiviation from certain kinds of plaster of old houses, where nitrate of lime is gradually generated. Liebig, in his profound work on the application of organic chemistry to Agriculture and Physiology, has rendered it highly probable, if not certain, that the nitric acid is formed by the oxidation of ammonia, which exists in the atmosphere, and is brought by absorption in contact with organic matters in a state of slow combustion or *eremacausis.* Ammonia is more easily oxidized than any other compound of nitrogen; probably because it contains hydrogen, the oxidation of which yields water, which is essential to the existence of nitric acid, and also because the hydrogen being oxidized, the nitrogen is presented in the nascent state to the atmospheric oxygen. Animal matters only act as a source of ammonia, and nitric acid may be formed where the decaying organic matter contains no nitrogen, from the ammonia present in the atmosphere. For the details of his argument, which in my opinion is quite conclusive, I must refer to the last English edition of that valuable work. The views of Liebig on nitrification have only been confirmed by all recent researches. That ammonia, derived from the putrefaction of organic matters, is always present in the atmosphere, is now an established fact; and it is probable that Liebig is correct in holding that the minute quantity of nitric acid found in the rain of thunderstorms is derived from the oxidation of that ammonia by the electric discharge, and not from the union of the oxygen and nitrogen of the atmosphere.

Nitrate of potassa is a colourless salt, which crystallizes readily in six-sided prisms. Its taste is saline, accompanied with an impression of coolness. It requires for solution seven parts of water at 60°, and its own weight of boiling water. It contains no water of crystallization, but its crystals are never quite free from water lodged mechanically within them. At 616° it undergoes the igneous fusion, and like all the nitrates, is decomposed by a red heat.

Nitre is chiefly employed in chemistry as an oxidizing agent, and in the formation of nitric acid. Its chief use in the arts is in making gunpowder, which is a mixture of nitre, charcoal, and sulphur. In the East Indies it is employed for the preparation of cooling mixtures; an ounce of powdered nitre dissolved in five ounces of water reduces its temperature by fifteen degrees. It possesses powerful antiseptic properties, and is therefore much employed in the preservation of meat and animal matters in general.

Nitrate of Soda.—This salt is analogous in its chemical properties to the preceding compound. It sometimes crystallizes in oblique rhombic prisms; but it more commonly occurs as an obtuse rhombohedron. (Brooke.) It is plentifully found in the soil of some parts of India; and at Atacama in Peru it covers large districts, and occurs in immense quantity. With charcoal and sulphur it forms a mixture which burns much slower than common gunpowder, and therefore cannot be substituted for nitre; but it may be advantageously used in the manufacture both of sulphuric and nitric acid. It is disposed to deliquesce in the air, and is soluble in twice its weight of cold water, and still more freely by the aid of heat.

Nitrate of Oxide of Ammonium.—It may be formed by neutralizing dilute nitric acid by carbonate of ammonia, and evaporating the solution. This salt may be procured in three different states, which have been described by Davy. (Researches concerning the Nitrous Oxide.) If the evaporation is conducted at a temperature not exceeding 100°, the salt is obtained in prismatic crystals isomorphous with nitre. If the solution is evaporated at 212°, fibrous crystals are procured; and if the heat be gradually increased to 300°, it forms a brittle compact mass on cooling. The fibrous and compact varieties still contain water, the former 8·2 per cent., and the latter 5·7. All these varieties deliquesce in a moist air, and are very soluble in water.

The change which nitrate of ammonia undergoes at a temperature varying between 400° and 500° has already been explained. When heated to 600°, it explodes with violence, being resolved into water, nitrous acid, binoxide of nitrogen, and nitrogen. The fibrous variety was found by Davy to yield the largest quantity of protoxide of nitrogen. From one pound of this salt he procured nearly three cubic feet of the gas.

Nitrate of Baryta.—This salt is much used as a reagent, and for preparing pure baryta. It is easily prepared by digesting the native carbonate, reduced to powder, in nitric acid diluted with 8 or 10 times its weight of water. The salt crystallizes readily by evaporation in transparent anhydrous octohedrons, and is very apt to decrepitate by heat unless previously reduced to powder. It requires 12 parts of water at 60°, and 3 or 4 of boiling water for solution, but is insoluble in alcohol. It undergoes the igneous fusion in the fire before being decomposed.

Nitrate of Strontia.—This salt may be made from strontianite in the same manner as the foregoing compound, to which it is exceedingly analogous. It commonly crystallizes in anhydrous octohedrons, which undergo no change in a moderately dry atmosphere, and are insoluble in alcohol; but sometimes it contains 30 per cent. of water of crystallization, and then assumes the form of the oblique prismatic system.

Nitrates of Lime and Magnesia.—These salts crystallize in hydrated prisms when their solutions are concentrated to the consistence of syrup, but the quantity of water which they contain is not ascertained. They deliquesce rapidly in the air, are very soluble in water, and are dissolved by alcohol, the nitrate of lime more freely than nitrate of magnesia.

Nitrate of Protoxide of Copper.—This salt is prepared by the action of nitric acid on copper. It crystallizes, though with some difficulty, in prisms of a deep blue colour, which are very soluble in water and alcohol, and deliquesce on exposure to the air. The green insoluble subsalt, procured by exposing the neutral nitrate to a heat of 400°, or by dropping an alkali into a solution of that salt, the latter being in excess, is a trinitrate, consisting of 3 eq. of oxide of copper, 1 eq. of acid, and 1 eq. of water. From the observations of Graham, the neutral salt contains 3 eq. of constitutional water, and therefore may be represented by the formula $CuO,NO_5,3HO$: from this it would appear that the subsalt is similarly constituted, being a nitrate of water with 3 eq. of constitutional oxide of copper. It is on this supposition represented by the formula $HO,NO_5,3CuO$. It is probable that the nitrates of lime and magnesia are similarly constituted, as has been shewn to be the case with nitric acid of sp. gr. 1·42. When heated to redness it yields pure oxide of copper.

Nitrate of Protoxide of Lead.—This salt is formed by digesting litharge in dilute nitric acid, and crystallizes readily in octohedrons, which are anhydrous and almost always opaque. It has an acid reaction, but is neutral in composition. It is much used in calico printing.

A dinitrate was formed by Berzelius by adding to a solution of the neutral nitrate a quantity of pure ammonia insufficient for separating the whole of the acid.

Nitrates of the Oxides of Mercury.—The protonitrate is conveniently formed by digesting mercury in nitric acid diluted with three or four parts of water, until the acid is saturated, and then allowing the solution to evaporate spontaneously in an open vessel. The solution always contains, at first, some nitrate of the peroxide; but if metallic mercury is left in the liquid, a pure protonitrate is gradually deposited. The salt thus formed has hitherto been regarded as the neutral protonitrate; but, according to the analysis of Dr. C. Mitscherlich (Pog. Annalen, ix. 387), it is a subsalt, in which the protoxide and acid are in the ratio of 208 to 36. This result, however, requires confirmation. The neutral protonitrate is said by C. Mitscherlich to be obtained in crystals, by dissolving the former salt in pure water acidulated with nitric acid, and evaporating spontaneously without the contact of metallic mercury or uncombined oxide. These salts dissolve completely in water slightly acidulated with nitric acid, but in pure water a small quantity of a yellow subsalt is generated.

When mercury is heated in an excess of strong nitric acid, it is dissolved with brisk effervescence, owing to the escape of binoxide of nitrogen, and transparent prismatic crystals of the pernitrate are deposited as the solution cools. When put into hot water it is resolved into a soluble salt, the composition of which is unknown, and into a yellow dinitrate of the peroxide. (An. de Ch. et Phys. xix.)

Nitrate of Oxide of Silver.—Silver is readily oxidized and dissolved by nitric acid diluted with two or three times its weight of water, forming a solution which yields transparent tabular crystals by evaporation. These crystals, which are anhydrous, undergo the igneous fusion at 426°, and yield a crystalline mass in cooling; but when the temperature reaches 600° or 700°, complete decomposition ensues, the acid being resolved into oxygen and nitrous acid, while metallic silver is left. When liquefied by heat, and received in small cylindrical moulds, it forms the *lapis infernalis* or *lunar caustic*, employed by surgeons as a cautery. The nitric acid appears to be the agent which destroys the animal texture, and the black stain is owing to the separation of oxide of silver. It is sometimes employed for giving a black colour to the hair, and is the basis of the indelible ink for marking linen.

The pure nitrate, whether fused or in crystals, is colourless and transparent, and does not deliquesce by exposure to the air; but common lunar caustic is dark and opaque, and dissolves imperfectly in water, owing to some of the nitrate being decomposed during its preparation. It is impure also, always containing nitrate of protoxide of copper, and frequently traces of gold. The pure salt is soluble in its own weight of cold, and in half its weight of hot water. It dissolves also in four times its weight of alcohol. Its aqueous solution, if preserved in clean glass vessels, especially with the addition of a minute quantity of free nitric acid, undergoes little or no change even in the direct solar rays; but when exposed to light, especially to sunshine, in contact with paper, the skin, or any organic substance, a black stain is quickly produced, owing to decomposition of the salt and reduction of its oxide to the metallic state. This change is so constant, that nitrate of oxide of silver constitutes an extremely delicate test of the presence of organic matter, and has been properly recommended as such by Dr. Davy. Its solution is always kept in the laboratory as a test for chlorine and hydrochloric acid.

Nitrate of oxide of silver, even after fusion, reddens vegetable colouring matters; but it is quite neutral in composition.

NITRITES.

Little is known with certainty concerning the compounds of nitrous acid with alkaline bases. Nitrite of potassa is formed by heating nitre to redness, and removing it from the fire before the decomposition is complete. On adding a strong acid to the product, red fumes of nitrous acid are disengaged, a character which is common to all the nitrites. The nitrite of soda, baryta, and strontia may be obtained in the same manner, and doubtless several others. Two nitrites of oxide of lead have been described in the Annales de Chimie, lxxxiii. by Chevreul and Berzelius. It is possible, however, that these compounds are hyponitrites.

CHLORATES.

The salts of chloric acid are very analogous to the nitrates. As the chlorates of the alkalies, alkaline earths, and most of the common metals, are composed of 1 eq. of chloric acid and 1 eq. of a protoxide, $MO + ClO_5$, it follows that the oxygen of the latter to that of the former is in the ratio of 1 to 5. The chlorates are decomposed by a red heat, nearly all of them being converted into metallic chlorides, with evolution of pure oxygen gas. They deflagrate with inflammable substances with greater violence than nitrates, yielding oxygen with such facility that an explosion is produced by slight causes. Indeed, the chlorate of ammonia, the base of which contains hydrogen, explodes when heated by itself; and its tendency to explode is so great, that when preserved it occasionally explodes spontaneously. A mixture of sulphur with three times its weight of chlorate of potassa explodes when struck between two hard surfaces. With charcoal and the sulphurets of arsenic and antimony, this salt forms similar explosive mixtures; and with phosphorus it detonates violently by percussion. One of the mixtures employed in the percussion caps for guns consists of sulphur and chlorate of potassa, with which a little charcoal or gunpowder is mixed; but, as the use of these materials is found corrosive to the lock, fulminating mercury is now generally preferred.

All the chlorates hitherto examined are soluble in water, excepting the chlorate of protoxide of mercury, which is of sparing solubility. These salts are distinguished by the action of strong hydrochloric and sulphuric acids, the former of which occasions the disengagement of chlorine and hypochlorous acid, and the latter of chlorous acid.

None of the chlorates are found native, and the only ones that require particular description are those of potassa and baryta.

Chlorate of Potassa.—This salt, formerly called *oxymuriate* or *hyper-oxymuriate of potash*, is best obtained by dissolving bleaching powder in water, and, after adding to the solution a proper quantity of chloride of potassium, 1 eq. KCl for 3 eq. of the pure bleaching compound, $CaO,ClO + CaCl$, boiling the whole nearly to dryness. The mass is then dissolved in hot water, filtered if necessary, and on cooling deposits a very large quantity of chlorate of potassa. As the bleaching powder of commerce contains a variable proportion of lime, it is better to dissolve a known weight of slaked lime in water by passing chlorine through it, by which means the lime is entirely converted into the bleaching compound. 6 eq. of lime, CaO,HO, and 6 eq. of chlorine, Cl_6, yield 3 eq. of the compound $CaO,ClO + CaCl$, and 6 eq. of water. Consequently, as 6 eq. of hydrate of lime are = 322, and 1 eq. of chloride of potassium is 75, for every 3 parts, by weight, of hydrate of lime dissolved, 1 part of chloride of potassium is added. The following equation shows the action of the chloride of potassium on the bleaching compound when they are boiled together:—$3(CaO, ClO + CaCl) + KCl = KO,ClO_5 + 6CaCl$. The salt is purified by recrystallization. It is colourless, and crystallizes in four and six-sided scales of a pearly lustre. Its forms are stated by Brooke to belong to the oblique prismatic system. It is soluble in sixteen times its weight of water at 60°, and in two and a half of boiling water. It is quite anhydrous, and when exposed to a temperature of 400° or 500° undergoes the igneous fusion. On increasing the heat almost to redness, effervescence ensues, and pure oxygen gas is disengaged, phenomena which have been explained in the section on oxygen. It can bear a heat of 600° without decomposition.

Chlorate of Baryta is of interest, as being the compound employed in the formation of chloric acid; and the readiest mode of preparing it is by the process of Wöhler. On digesting for a few minutes a concentrated solution of chlorate of potassa with a slight excess of silicated hydrofluoric acid, the alkali is precipitated in the form of an insoluble double fluoride of silicium and potassium, while chloric acid remains in solution. The liquid after filtration is neutralized by carbonate of baryta, which throws down the excess of silicated hydrofluoric acid, and chlorate of baryta is left in solution. By evaporation it yields prismatic crystals, which require for solution 4 times their weight of cold, and a still smaller quantity of hot water. They are composed of 76·7 parts or 1 eq. of baryta, 75·42 or 1 eq. of chloric acid, and 9 or 1 eq. of water.

Perchlorates.—The neutral proto-salts of perchloric acid consist of 1 eq. of acid and base, as is expressed by the formula $MO + Cl_2O_7$. Most of these salts are deliquescent, very soluble in water, and soluble in alcohol: four only were found by Serullas to be not deliquescent,—the perchlorates of potassa, ammonia, protoxide of lead, and protoxide of mercury. When heated to redness they yield oxygen gas and metallic chlorides; and they are distinguished from the chlorates by not acquiring a yellow tint on the addition of hydrochloric acid. The perchlorate of potash is prepared from the chlorate by the action of heat or sulphuric acid, as already mentioned. It is the most insoluble of the perchlorates, and on this account perchloric acid precipitates potassa from its salts, being a test of about the same delicacy as tartaric acid. The other perchlorates are made by neutralizing the base with perchloric acid. The solubility in alcohol of the perchlorates of baryta, soda, and oxide of silver is a property which the analytical chemist may avail himself of in analysis for the separation of potassa and soda from each other.

CHLORITES.

The alkaline salts of chlorous acid are readily made, as mentioned at page 281, by transmitting a current of chlorous acid gas into a solution of the pure alkalies. All that have as yet been examined are soluble in water, and are remarkable for their highly bleaching and oxidizing properties. By the latter properties, and the evolution of chlorous acid on the addition of any of the stronger acids, their presence is readily recognized.

Hypochlorites.—The hypochlorites may be produced by the action of chlorine gas on the salifiable bases. The most important of them is the hypochlorite of lime, the well-known bleaching compound, which has commonly been described as the oxymuriate or chloride of lime. When slaked lime is suspended in a large quantity of water, and chlorine passed through the mixture, the lime, if pure, is at last entirely dissolved, and the solution contains the bleaching compound, free from excess of lime. Its formation is thus explained:—$2CaO + Cl_2 = CaO, ClO + CaCl$. It is prepared for commercial purposes by exposing thin strata of recently slaked lime in fine powder to an atmosphere of chlorine. The gas is absorbed in large quantity, and the chloride of calcium and hypochlorite of lime are produced in equivalent proportions as above described, but are mixed with a variable proportion of free lime in the commercial bleaching powder.

It is a dry white powder, which smells faintly of chlorine, and has a strong taste. It dissolves partially in water, and the solution possesses powerful bleaching properties, and contains both chlorine and lime; while the undissolved portion is hydrate of lime, retaining a small quantity of chlorine. The aqueous solution, when exposed to the atmosphere, is gradually decomposed; chlorine is set free, and carbonate of lime generated. On boiling the liquid, chloride of calcium and chlorate of lime are formed; and, as above mentioned, by adding chloride of potassium, chlorate of potassa is obtained, the chlorate of lime and chloride of potassium exchanging metals. This is the best method of preparing chlorate of potassa. By long keeping, the dry chloride appears to undergo a similar change,—at least chloride of calcium is produced in large quantity. It is also decomposed by a strong heat: at first, chlorine is evolved; but pure oxygen is afterwards disengaged, and chloride of calcium remains in the retort, mixed with free lime.

The composition of chloride of lime was first carefully investigated by Dalton,* and it has since been analyzed by Thomson,† Welter,‡ and Ure.§ The three first-mentioned chemists infer from their researches that bleaching powder is a hydrated *subchloride* or *dichloride* of lime, in which one equivalent of chlorine is united with two equivalents of lime. They are also of opinion, that, on mixing this dichloride with water, the chloride is dissolved, and one eq. of lime separated as an insoluble powder. Dr. Ure, on the contrary, denies that bleaching powder is a dichloride, and maintains that the elements of this powder do not constitute a regular atomic combination. He found that the quantity of chlorine absorbed by hydrate of lime is variable, depending not only on the pressure and degree of exposure, but on the quantity of water present. From these experiments it appears that the commercial bleaching powder is essentially a hypochlorite with single equivalents of its elements, combined, as is now admitted, with an equivalent of chloride of calcium, but mixed with variable quantities of hydrate of lime.

According to Millon, bleaching powder is an oxychloride of calcium, $CaO,ClO + CaCl. = 2\left\{Ca\begin{matrix}Cl\\O\end{matrix}\right\}$ It is now certain, that even if hypochlorites exist, the bleaching compounds of lime, potash, and soda contain the chlorides of these metals as an essential constituent, according to the first of the above formulæ. But according to the view of Millon, these compounds must be viewed as oxychlorides, corresponding to the peroxides of the metals, in which part of the oxygen is replaced by chlorine. But, although there is some plausibility in the views of Millon, the experiments of Detmer have shewn that some of his assumptions are erroneous; and chemists are now generally disposed to consider the bleaching compound of lime as a compound of hypochlorite of lime with chloride of calcium, $CaO,ClO + CaCl$.

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* Annals of Philosophy, i. 15, and ii. 6.

† Ibid. xv. 401.

‡ Ann. de Ch. et Ph. vol. viii.

§ Quarterly Journal, xiii. 1.

Several methods have been proposed for estimating the value of different specimens of bleaching powder. Perhaps the most convenient for the artist is that of Welter, which consists in ascertaining the power of the bleaching liquid to deprive a solution of indigo of known strength of its colour; and directions have been drawn up by Gay-Lussac for enabling manufacturers to employ this method with accuracy. (Annals of Philosophy, xxiv. 218.) For analytical purposes, the best method is to decompose chloride of lime, confined in a glass tube over mercury, by means of hydrochloric acid. Chloride of calcium is generated, and the chlorine being set free, its quantity may easily be measured.

IODATES.

From the close analogy in the composition of chloric and iodic acids, it follows that the general character of the iodates must be similar to that of the chlorates. Thus in all neutral protiodates the oxygen contained in the oxide and acid is in the ratio of 1 to 5. They form deflagrating mixtures with combustible matters; and on being heated to low redness, oxygen gas is disengaged and a metallic iodide remains. As the affinity of iodine for metals is less energetic than that of chlorine, many of the iodates part with iodine as well as oxygen when heated, especially if a high temperature is employed.

The iodates are easily recognized by the facility with which their acid is decomposed by deoxidizing agents. Thus, the sulphurous, phosphorous, hydrochloric, and hydriodic acids deprive iodic acid of its oxygen, and set iodine at liberty. Hydrosulphuric acid not only decomposes the acid of these salts, but occasions the formation of hydriodic acid by yielding hydrogen to the iodine. Hence an iodate of potassa may be converted into the iodide by transmitting a current of hydrosulphuric acid gas through its solution. None of the iodates have been found native. They are all of very sparing solubility, or actually insoluble in water, excepting the iodates of the alkalies.

Iodate of Potassa.—This salt may be procured by adding iodine to a concentrated hot solution of pure potassa, until the alkali is completely neutralized. The liquid, which contains an iodate and iodide, is evaporated to dryness by a gentle heat, and the residue, when cold, is treated by repeated portions of boiling alcohol. The iodate, which is insoluble in that menstruum, is left, while the iodide of potassium is dissolved. A better process has been recommended by M. Henry, jun., founded on the property which iodide of potassium possesses, of absorbing oxygen while in the act of escape from decomposing chlorate of potassa. For this purpose iodide of potassium is fused in a capacious hessian crucible, and while, after removal from the fire, it is yet semi-fluid, successive portions of pulverized chlorate of potassa are projected into it, stirring well after each addition. The materials froth up considerably, and when the action is over, a white, opaque, cellular mass remains, easily separable from the crucible: tepid water dissolves out the chloride of potassium, and leaves the iodate. Convenient proportions are one part of iodide of potassium and rather more than one and a half of chlorate of potassa. (Journ. de Pharmacie, July 1832.)

All the insoluble iodates may be procured from this salt by double decomposition. Thus, iodate of baryta may be formed by mixing chloride of barium with a solution of iodate of potassa.

A biniodate of potassa has been described by Serullas. It is formed by incompletely neutralizing a hot solution of chloride of iodine with potassa or its carbonate, and setting it aside to cool. A peculiar compound of chloride of potassium and biniodate of potassa falls; but on dissolving this substance, filtering and exposing the solution to a temperature of 77°, the biniodate is gradually deposited in right rhombic prisms terminated by dihedral summits. It is soluble in 75 times its weight of water at 59°.

A teriodate may be formed by mixing a large excess of sulphuric acid with a moderately dilute solution of iodate of potassa. On evaporating at 77°, the teriodate is deposited in regular rhomboidal crystals, which require 25 times their weight of water at 60° for solution.

Serullas states that the compound of chloride of potassium and biniodate of potassa, above mentioned, may be formed by the action of hydrochloric acid on iodate of potassa. By spontaneous evaporation it is obtained, sometimes in brilliant, transparent, elongated prisms, and at other times in hexagonal laminæ; but generally it crystallizes in right quadrangular prisms with their lateral edges truncated, and terminated by four-sided summits. (An. de Ch. et Ph. xliii. 113.)

Bromates.—These compounds have many characters in common with the chlorates and iodates; but hitherto they have been but partially examined.

PHOSPHATES.

In studying these salts the reader must bear in mind the facts detailed concerning the phosphoric acids in a previous section. There are three acids, the monobasic or metaphosphoric, the bibasic or pyrophosphoric, and the tribasic or common phosphoric acid. Graham considers these three acids as isomeric modifications of the same acid, differing only in the amount of combined or basic water, and in their tendency to unite with 1, 2, and 3 eqs. of base respectively, to form neutral salts. Graham's view may be represented in a tabular form, as follows:—

Metaphosphoric Acid.	Pyrophosphoric Acid.	Common Phosphoric Acid.
PO_5,HO	$PO_5,2HO$	$PO_5,3HO$
Metaphosphates.	Pyrophosphates.	Common Phosphates.
PO_5,MO	$PO_5,2MO$	$PO_5,3MO$
	$PO_5\left\{\begin{matrix}MO\\HO\end{matrix}\right.$	$PO_5,\left\{\begin{matrix}2MO\\HO\end{matrix}\right.$
		$PO_5\left\{\begin{matrix}MO\\2HO.\end{matrix}\right.$

It will be seen that the metaphosphoric acid forms one series of salts only, while the pyrophosphoric acid forms two, and the common phosphoric acid three series of salts. In the second series of pyrophosphates, and in the second and third series of common phosphates, the basic water is only partially replaced by a fixed alkaline base. All these salts are neutral in composition, as is shewn by the fact that the three salts, PO_5,NaO, $PO_5,2NaO$, and $PO_5,3NaO$, each yield a different precipitate with nitrate of silver, and yet in each case the supernatant liquid is found to be neutral. In those series in which the fixed base is partly replaced by water, the water is evidently basic; and for our knowledge of this important fact we are indebted chiefly to Graham. But, although the above view enables us to understand the differences in composition of the different classes of phosphates, it fails to afford any explanation of these differences. If, as Graham thinks, the acid in all is the same acid, PO_5, combined with different proportions of water or of fixed base, we ask in vain why the acid PO_5 should at one time combine with 1 eq. of water or of fixed base, at another with 2, and at another with 3. To say, that when the acid is made to combine with 3 eq. of water or fixed base, it retains the tendency to do so, and that when it is compelled to unite with 2 or with 1 eq. it retains the tendency to do so, is no explanation: it is merely stating the fact in different words. Besides, we know other acids which combine with water in different proportions, and yet invariably combine with the same proportion of base. Sulphuric acid, for example, combines with three different proportions of water, yielding the compounds SO_3,HO, $SO_3,2HO$, and $SO_3,3HO$; but each of these, when neutralized by soda, yields the same salt, NaO,SO_3. It is plain, therefore, that the mere fact of the acid uniting with water in different proportions does not give such a tendency as Graham assumes to unite with bases in the same proportion.

On the other hand, Liebig, proceeding on the fact that the three phosphoric acids differ essentially in properties, has endeavoured to trace these differences to differences in composition. That the three acids differ in properties is evident: for metaphosphoric, or, as Liebig calls it, monobasic phosphoric acid, coagulates albumen, and precipitates the nitrates of baryta and silver; pyrophosphoric or bibasic phosphoric acid does not coagulate albumen, and it does not precipitate nitrate of silver unless it be first combined with an alkali, when it causes a granular white precipitate in that salt. Finally, common, or tribasic phosphoric acid does not precipitate albumen, and, when combined with an alkali, gives a yellow precipitate with nitrate of silver. We are acquainted with no instance in which a mere difference in the proportion of water combined with the same acid produces properties so distinct, and the natural conclusion is, that the acids are essentially different. If so, we should of course expect each to retain its essential characters in its salts, and this is found to be the case. But what is the difference between them? Liebig is of opinion that they are not, as Graham supposes, hydrates of the same oxygen acid, but three distinct hydrogen acids. This view has already, in the section introductory to the salts, been explained in reference to oxygen acids in general, including the phosphoric acids. It is here put into a tabular form, in order that the reader may compare it with that of Graham above given:—

Monobasic Phosphoric Acid.	Bibasic Phosphoric Acid.	Tribasic Phosphoric Acid.
PO_6,H	PO_7,H_2	PO_8,H_3
Monobasic Phosphates.	**Bibasic Phosphates.**	**Tribasic Phosphates.**
PO_6,M	PO_7,M_2	PO_8,M_3
	$PO_7\left\{\begin{matrix}M\\H\end{matrix}\right.$	$PO_8\left\{\begin{matrix}M_2\\H\end{matrix}\right.$
		$PO_8\left\{\begin{matrix}M\\H_2\end{matrix}\right.$

On this view, the formulæ of the three acids indicate an essential difference of composition, inasmuch as they contain different amounts of replaceable hydrogen; and it is precisely because the amount of replaceable hydrogen differs in the three acids, that they differ in neutralizing power, the monobasic acid, like sulphuric acid, nitric acid, and many others, being neutralized when the 1 eq. of replaceable hydrogen it contains is replaced by 1 eq. of a metal; while the bibasic and tribasic acids require 2 and 3 eqs. of metal respectively to yield neutral salts. This view, therefore, involves the doctrine of polybasic acids; whereas the other view only involves the fact in this case, without attempting to explain it. There is but one circumstance which at first appears to tell in favour of Graham's view, namely, that the three acids readily pass into one another when dissolved in water. But if we consider their composition, and that water contains the very elements in which they differ, we shall see that the fact of their convertibility is no proof of the accuracy of Graham's view. Moreover, the change takes place very slowly, unless under the influence of heat; and, even in that case, it requires time.

We shall, therefore, describe the phosphates in three distinct forms: —the monobasic, bibasic, and tribasic phosphates.

MONOBASIC PHOSPHATES.

Syn. Metaphosphates.—The only salts of this kind hitherto described are the following:—

Metaphosphate of Soda.—When the pyrophosphate or acid bibasic phosphate of soda is heated to low redness, it fuses, and on cooling becomes a transparent glass, which deliquesces in a damp air, and is very soluble. The solution has a feeble acid reaction. When mixed with nitrate of oxide of silver, the monobasic phosphate of that oxide falls in gelatinous flakes, wholly unlike the pyrophosphate, and aggregates together as a soft solid when heated to near 212°. The metaphosphate of soda does not change by keeping, and has not hitherto been made to crystallize. When its solution is evaporated, and kept for some time at 400°, it is reconverted into the acid bibasic phosphate of soda. All the preceding facts are drawn from Graham's essay. (Phil. Trans., 1833, Part ii.)

Metaphosphate of Baryta falls in gelatinous flakes on adding metaphosphate of soda to a solution of chloride of barium, the latter being in excess as the soda salt dissolves the precipitate. By long-continued boiling monobasic metaphosphate of baryta is at length dissolved, and at the same time converted into a tribasic phosphate.

The metaphosphate of silver is obtained by precipitation, as above stated. When put, while moist, into boiling water, part of its acid is removed, and the submetaphosphate is generated.

In describing the method of extracting pure phosphoric acid from bones, a salt was mentioned, described by Gregory as an anomalous phosphate of magnesia, but which had since been shewn by Maundrell to contain soda, a base not previously found in bones. The analysis of this salt leads to the formula $NaO,3MgO,4PO_5$: it is probably $NaO,PO_5 + 3(MgO,PO_5)$, a double monobasic phosphate of soda and magnesia.

BIBASIC PHOSPHATES.

Syn. Pyrophosphates.—These salts were discovered by Clark, and have been studied by Stromeyer and Graham. That modification of phosphoric acid termed *pyrophosphoric acid* is procured by forcing with the aid of heat phosphoric acid to combine with 2 eq. either of water or some fixed base. The only pyrophosphates which have as yet been studied are those of soda and oxide of silver.

Pyrophosphate of Soda.—This is the compound first prepared by Clark from the rhombic phosphate, by expelling its basic water. When the residual mass is dissolved in water and set to evaporate, crystals are obtained, having the outline of an irregular six-sided prism, derived from a rhombic prism. These crystals are permanent in the air, much less soluble in water than the original rhombic phosphate, and quite neutral to test paper. Ignited with carbonate of soda, a phosphate is reproduced, because the acid is forced to unite with 3 eq. of a base.

Pyrophosphate of soda is permanent both in crystals and in solution in the cold; but by long boiling, or quickly when boiled with an acid, a phosphate is reproduced. With a salt of lead it yields a white pyrophosphate of oxide of lead; and on washing the precipitate and decomposing by hydrosulphuric acid gas, a solution of pyrophosphoric acid is obtained, which again forms pyrophosphate of soda when neutralized with soda.

The oxides of most metals of the second class yield with pyrophosphoric acid insoluble or sparingly soluble salts, which may be prepared by double decomposition with pyrophosphate of soda. It should be held in view, however, as Stromeyer has remarked, that most of these salts are more or less soluble in an excess of pyrophosphate of soda; and that some of them, such as the pyrophosphate of the oxides of lead, copper, nickel, cobalt, uranium, bismuth, manganese, and mercury, are dissolved by it with great facility. Its formula is $2NaO,PO_5$; or Na_2,PO_7.

Acid Pyrophosphate of Soda and Water.—This salt is formed by exposing the acid triphosphate to a heat of 400°, when it loses one-half of its basic water, and acquires the character of a pyrophosphate.

This salt dissolves readily in water, has an acid reaction, and has not been obtained in crystals. Its formula is

$$NaO,HO,PO_5\text{ ; or }\left.\begin{matrix}Na\\H\end{matrix}\right\}PO_7.$$

When the preceding salt, $NaO,HO + PO_5$, is heated to 600° or a little higher, it loses its basic water, and yet the acid does not lose the character of pyrophosphoric acid. It is left, therefore, as a simple pyrophosphate of soda, $NaO + PO_5$. On adding water part of it dissolves, and part is left as an insoluble white powder. The solution is *quite neutral to test paper;* but on adding nitrate of oxide of silver, the dipyrophosphate of that oxide falls, and free nitric acid remains in solution. The soluble and insoluble pyrophosphate of soda appear identical in composition, and the former at a heat just short of redness may be wholly converted into the latter. There is something apparently anomalous about this salt. That it should be neutral to test paper, while the preceding salt, containing an additional eq. of basic water, is strongly acid, excites the suspicion that possibly the insoluble and soluble portions may differ in composition. At all events, this salt demands further study.

Pyrophosphate of Oxide of Silver.—This salt is readily formed by double decomposition with dipyrophosphate of soda and nitrate of oxide of silver, the residual liquid being quite neutral to test paper. It falls as a snow-white granular precipitate, which fuses readily at a heat short of incandescence into a dark brown liquid, which becomes a crystalline enamel on cooling.

TRIBASIC PHOSPHATES.

Syn. Common Phosphates, or Phosphates.—The phosphates, except those of the pure alkalies, are either sparingly soluble or insoluble in water; but they are all dissolved by dilute nitric or phosphoric acid, being converted into the soluble phosphates. All the phosphates with 3 eq. of fixed and strong bases bear a red heat without change; but the acid phosphates, to judge from experiments on the soda salts, are converted into metaphosphates and pyrophosphates. Most of the phosphates of the second class of metals are resolved into phosphurets by the conjoint agency of heat and combustible matter. The phosphates of the alkalies are only partially decomposed under these circumstances, and the phosphates of baryta, strontia, and lime undergo no change.

The presence of a soluble phosphate may be distinguished by the tests already mentioned for phosphoric acid. The insoluble phosphates are decomposed when boiled with a strong solution of carbonate of potassa or soda, the acid uniting with the alkali so as to form a soluble phosphate: the earthy phosphates, indeed, are decomposed with difficulty, requiring continued ebullition, and should preferably be fused with an alkaline carbonate, like an insoluble sulphate.

Several phosphates are met with in nature, such as those of lime, alumina, and the oxides of manganese, iron, uranium, copper, and lead.

The composition of the principal phosphates is given in the following table:—

Names.	Base.			Acid.		Equiv.	Formulæ.
Triphosphate of Soda . .		93·9	3 eq.	+ 71·4	1 eq.	=165·3	$3NaO+PO_5$.
Do. in crystals with 216 or 24 eq. of water . .						=381·3	
Triphosph. Soda and Basic Water .	Soda	62·6	2 eq.	+ 71·4	1 eq.	=143	$2NaO,HO+PO_5$.
	Water	9	1 eq.				
Do. in crystals with 216 or 24 eq. of water . .						=359	
Do. . . . 135 or 15 eq. of water . .						=278	
Acid Triphosph. Soda and Basic Water	Soda	31·3	1 eq.	+ 71·4	1 eq.	=120·7	$NaO,2HO+PO_5$.
	Water	18	2 eq.				
Do. in crystals with 18 or 2 eq. of water . . .						=138·7	
Triphosphate of Potassa . .		141·45	3 eq.	+ 71·4	1 eq.	=212·85	$3KO+PO_5$.
Triphosph. of Potassa and Basic Water	KO	94·3	2 eq.	+ 71·4	1 eq.	=174·7	$2KO,HO+PO_5$.
	HO	9	1 eq.				
Acid Triphosphate ditto . .	Potassa	47·15	1 eq.	+ 71·4	1 eq.	=136·55	$KO,2HO+PO_5$.
	Water	18	2 eq.				
Triphosph. of Soda, Oxide Ammonium, and Basic Water	Soda	31·3	1 eq.	+ 71·4	1 eq.	=137·85	$NaO,H_4NO,HO+PO_5$.
	Ox. Am.	26·15	1 eq.				
	Water	9	1 eq.				
Do. in crystals with 72 or 8 eq. of water . . .						=209·85	
Triphosph. of oxide of Am. & Basic Water	Ox. Am.	52·30	2 eq.	+ 71·4	1 eq.	=132·70	$2H_4NO,HO+PO_5$.
	Water	9	1 eq.				
Acid Triphosphate ditto . .	Ox. Am.	26·15	1 eq.	+ 71·4	1 eq.	=115·55	$H_4NO,2HO+PO_5$.
	Water	18	2 eq.				
Bone Phosphate of Lime .		228	8 eq.	+214·2	3 eq.	=442·2	$8CaO+3PO_5$.
Triphosphate do. . .		85·5	3 eq.	+ 71·4	1 eq.	=156·9	$3CaO+PO_5$.
Triphos. of Lime and Basic Water .	Lime	57	2 eq.	+ 71·4	1 eq.	=127·4	$2CaO,HO+PO_5$.
	Water	9	1 eq.				
Acid Triphos. do.	Lime	28·5	1 eq.	+ 71·4	1 eq.	=117·9	$CaO,2HO+PO_5$.
	Water	18	2 eq.				

Phosphate of Soda.—This salt, described by Graham as the *subsesquiphosphate*, is made by adding pure soda to a solution of the succeeding compound, until the liquid feels soapy to the fingers, an excess of soda not being injurious. The liquid is then evaporated until a pellicle appears, and the crystals which form on cooling are quickly redissolved in water and recrystallized. Though the crystals do not change in the air, the solution absorbs carbonic acid, and the resulting carbonate of soda adheres to the triphosphate.

This salt crystallizes in colourless six-sided slender prisms, which have a strong alkaline taste and reaction, require 5 times their weight of water at 60°, and still less of hot water, for solution, and at 170° fuse in their water of crystallization. They may be exposed to a red heat without losing the characters of a phosphate. The feeblest acids deprive the salt of one-third of its soda. Its formula is $3NaO,PO_5$, or Na_3,PO_8+24 aq.

When this salt is mixed in solution with nitrate of oxide of silver in excess, there is an exact interchange of elements, such that

1 eq. Phosphate of Soda $3NaO+PO_5$	yield	1 eq. Phosph. of Silver $3AgO+PO_5$
and 3 eq. Nitrate of Silver $3(AgO+NO_5.)$		and 3 eq. Nitrate of Soda $3(NaO+NO_5)$.

The resulting solution is therefore quite neutral. The phosphate of oxide of lead, and other insoluble phosphates, may be prepared in like manner.

Common Phosphate of Soda and Basic Water.—This salt is the most common of the phosphates, being manufactured on a large scale by neutralizing with carbonate of soda the acid phosphate of lime procured by the action of sulphuric acid on burned bones. It is generally described as a neutral phosphate of soda, and for distinction's sake is sometimes termed *rhombic phosphate*, from its crystals having the form of oblique rhombic prisms.

This salt crystallizes best out of an alkaline solution; but however prepared, it is always alkaline to test paper, and requires a considerable quantity of acid before losing its alkalinity. The crystals effloresce on exposure to the air, and require four times their weight of cold, and twice their weight of hot water for solution. It often contains traces of sulphuric acid, from which it may be purified by repeated solution and crystallization. When mixed with nitrate of oxide of silver, the interchange of elements is such that

1 eq. Rhombic. Phos. $2NaO,HO+PO_5$	yield	1 eq. Triphosp. of Silver $3AgO+PO_5$
and 3 eq. Nitrate of Silver $3(AgO+NO_5)$		and 2 eq. Nitrate of Soda $2(NaO+NO_5)$.

The yellow phosphate of oxide of silver falls exactly as with the former salt, but 1 eq. of nitric acid is left free in the solution.

When a solution of the rhombic phosphate is evaporated at a temperature of 90°, it crystallizes with 14 instead of 24 equivalents of water, and the crystals differ, as might be expected, from the other salt in figure, and are permanent in the air. Both salts lose their basic water at a red heat, and are converted into a pyrophosphate. Its formula, in crystals, is $2NaO,HO+PO_5+24$ aq.; or $\left.\begin{matrix}Na_2\\H\end{matrix}\right\}+PO_8+$ 24 aq.

Acid Phosphate of Soda and Water.—This salt, commonly called *biphosphate of soda* from its acid reaction, may be formed by adding phosphoric acid to a solution of carbonate of soda, or to either of the preceding phosphates, until it ceases to give a precipitate with chloride of barium. Being very soluble in water, the solution must be concentrated in order that it may crystallize. This salt is capable of yielding two different kinds of crystals without varying its composition. The more unusual form, isomorphous with binarseniate of soda, is a right rhombic prism, the smaller lateral edge of which is 78° 30′, terminated by pyramidal planes. The form of its ordinary crystals is a right rhombic prism, the larger angle of which is 93° 54′.

The crystals of this salt consist of $NaO,2HO,PO_5 + 2HO$. When heated to 212°, the water of crystallization is expelled, and the anhydrous salt remains, still yielding a yellow precipitate with silver when neutralized by ammonia; but if exposed to a heat of 400°, it loses half its basic water, being reduced to NaO,HO,PO_5, and has the character of pyrophosphate of soda. At a red heat it is converted into metaphosphate of soda.

Tribasic Phosphate of Potassa.—Graham formed this salt by adding caustic potassa in excess to a solution of phosphoric acid, as well as by fusing phosphoric acid with a slight excess of carbonate of potassa. He obtained it in acicular crystals, which were very soluble in water, but not deliquescent.

Tribasic Phosphate of Potassa and Basic Water.—This salt may be prepared by neutralizing the superphosphate of lime from bones with carbonate of potassa. It is deliquescent, and has not been obtained in regular crystals.

Acid Phosphate of Potassa and Basic Water may be formed by adding phosphoric acid to carbonate of potassa until the liquid ceases to give a precipitate with chloride of barium, and setting it aside to crystallize. The crystals belong to the square prismatic system, and they usually occur in square prisms terminated by the planes of an octohedron. They are acid to test paper.

When this compound is neutralized by carbonate of soda, and the solution set to crystallize, a phosphate of soda and potassa is deposited in crystals, the form of which is an oblique rhombic prism, which frequently occurs without any modification.

Tribasic Phosphate of Soda and Oxide of Ammonium and Basic Water.—This salt is easily prepared by mixing together 1 eq. of hydrochlorate of ammonia and 2 eq. of the rhombic phosphate of soda, each being previously dissolved in a small quantity of boiling water. As the liquid cools, prismatic crystals of the double phosphate are deposited, while chloride of sodium remains in solution. Their form is an oblique rhombic prism. This salt has been long known by the name of *microcosmic salt*, and is much employed as a flux in experiments with the blowpipe. When heated it parts with its water and ammonia, and a very fusible metaphosphate of soda remains. Its formula is $NaO,$

$$NH_4O,HO + PO_5 + 8\ aq.;\ or\ \left.\begin{matrix}Na\\NH_4\\H\end{matrix}\right\} + PO_8 + 8\ aq.$$

Tribasic Phosphate of Ox. Ammonium and Basic Water.—This salt is formed by adding ammonia to concentrated phosphoric acid until a precipitate appears. On applying heat, the precipitate is dissolved; and on abandoning the solution to itself, the neutral salt crystallizes. The form of the crystals is an oblique rhombic prism, the smaller angle of which is 84° 30′. They often occur in rhombic prisms with diedral summits. (Mitscherlich.)

The acid triphosphate is made in the same manner as the preceding triphosphate of potassa. The crystals are less soluble than the preceding salt, and undergo no change on exposure to the air. Their form is an octohedron with a square base; but the right square prism, terminated by the faces of the octohedron, is the most frequent.

Phosphates of Lime.—The peculiar compound called the *bone phosphate* exists in bones after calcination, and falls as a gelatinous precipitate on pouring chloride of calcium into a solution of the rhombic phosphate of soda, or on adding ammonia to a solution of any phosphate of lime in acids.

Its formula is $8CaO + 3PO_5$, according to Berzelius. Fuchs considers it to be $3CaO + PO_5$, which is a tribasic salt, exactly analogous to the corresponding salts of soda and potassa. But Berzelius, in his latest analyses, has obtained the same results as before, leading to the apparently anomalous formula $8CaO + 3PO_5$. This may possibly be a compound of a tribasic and a bibasic salt, $2(3CaO,PO_5) + 2CaO,PO_5$. If it contains 1 eq. of water, it will be $2(3CaO,PO_5) + (2CaO,HO,PO_5)$, entirely tribasic. Bone-earth is very soluble in acids, and is precipitated by alkalies. It is slightly dissolved by ammoniacal salts. Two recent discoveries, that of the very considerable amount of fluoride of calcium present in bone-earth, and that of the occurrence of soda in bone-earth, also in considerable quantity, render a new investigation of this important compound necessary.

Triphosphate of Lime and Basic Water, commonly called *neutral phosphate*, falls as a granular precipitate, consisting of fine crystalline particles, when the rhombic phosphate of soda is added in solution drop by drop to chloride of calcium in excess. The residual liquid reddens litmus. owing to a small quantity of triphosphate of lime being generated.

Triphosphate of Lime cannot be formed by precipitation, but occurs in hexagonal prisms in the mineral called *apatite.*

Acid Triphosphate of Lime and Basic Water, called the *biphosphate* from its acid reaction, is formed by dissolving either of the preceding salts in a slight excess of phosphoric acid. The compound is deliquescent, very soluble, and crystallizes with great difficulty. It exists in the urine. The solution formed by the action of sulphuric acid on bones is probably a compound of lime with 2 or more eq. of phosphoric acid, being really a *superphosphate.*

Triphosphate of Magnesia and Basic Water.—It is formed by mixing together hot saturated solutions of the rhombic phosphate of soda and sulphate of magnesia, and separates on cooling in small crystals, which contain 13 eq. of water to one of the salt. The triphosphate of magnesia is principally formed when the solutions are intermixed in the cold. These salts have been but little examined.

The *phosphate of ammonia and magnesia* subsides as a pulverulent granular precipitate from neutral or alkaline solutions, containing phosphoric acid, ammonia, and magnesia. It is readily dissolved by acids, and is sparingly soluble in pure water, especially when carbonic acid is present; but it is insoluble in a solution of most neutral salts, such as hydrochlorate of ammonia. It constitutes one variety of urinary concretions. According to Berzelius it consists of

Phosphoric Acid . .	71·4	1 eq.	PO_5.
Magnesia . . .	41·4	2 eq.	$2MgO$.
Ammonia . . .	34·3	2 eq.	$2H_3N$.
Water . . .	90	10 eq.	$10HO$.

The mode in which these elements are arranged is unknown. When heated to redness it loses its water and ammonia, and the residue is diphosphate of magnesia, which contains 36·67 per cent. of pure magnesia. At a strong red heat it fuses, and appears when cold as a white enamel.

When the materials for forming the preceding salt are mixed while hot, small acicular crystals subside on cooling, which are said by Berzelius to contain less of the two bases than the other salt.

Phosphates of Protoxide of Lead.—The triphosphate is precipitated when acetate of oxide of lead is mixed with a solution of the rhombic phosphate of soda, acetic acid being set free. The phosphate with basic water is best formed by adding the rhombic phosphate of soda gradually to a hot solution of chloride of lead. The nitrate should not be used for the purpose, as it combines with the precipitate. Both these phosphates are white, and are frequently formed at the same time. The latter fuses readily into a yellow bead, which in cooling acquires crystalline facettes.

Tribasic Phosphate of Oxide of Silver.—This compound subsides, of a characteristic yellow colour, when the rhombic phosphate of soda is mixed in solution with nitrate of oxide of silver, nitric acid being set free at the same time. It is apt to retain some of the nitrate in combination. This salt is very soluble in nitric and phosphoric acid, forming the soluble phosphate, and in ammonia. By exposure to light it is speedily blackened; but when protected from this agent, it yields on drying an anhydrous yellow powder, which has a sp. gr. of 7·321. (Stromeyer.) Its colour changes on the application of heat to a reddish-brown, but its original tint returns on cooling. It bears a red heat without fusion: at a white heat it fuses, and if kept for some time in a fused state a portion of pyrophosphate is generated. Its formula is $3AgO,PO_5$ or Ag_3,PO_8.

ARSENIATES.

Arsénic acid resembles the phosphoric in composition and in many of its properties, but as far as is yet known is only capable of forming tribasic salts. Those which contain 2 eq. of basic water are, like the phosphates, soluble in water and redden litmus, whence they are commonly considered as bisalts. If only 1 eq. of basic water be present, in which the oxygen of the alkaline base and acid is as 2 to 5, the salt is usually termed a neutral arseniate. When no basic water is present, the salt is usually described as a sub-arseniate. Both the neutral and the sub-arseniates, however, give, with nitrate of silver, the same brick-red precipitate, which is the tribasic arseniate of silver. The two last series of salts, except those with the alkalies, are of sparing solubility in water; but they are dissolved by phosphoric or nitric acid, as well as most acids which do not precipitate the base of the salt.

Many of the arseniates bear a red heat without decomposition, or being otherwise modified in their characters; but they are all decomposed when heated to redness along with charcoal, metallic arsenic being set at liberty. The arseniates of the fixed alkalies and alkaline earths require a rather high temperature for reduction; while the arseniates of the second class of metals, as of lead and copper, are easily reduced in a glass tube by means of a spirit-lamp without danger of melting the glass. Of all the arseniates, that of oxide of lead is the most insoluble.

The soluble arseniates are easily recognized by the tests described in the section on Arsenic; and the insoluble arseniates, when boiled in a strong solution of the fixed alkaline carbonates, are deprived of their acid, which may then be detected in the usual manner. The free alkali, however, should first be exactly neutralized by pure nitric acid.

The arseniates of lime, and of the oxides of nickel, cobalt, iron, copper, and lead, are natural productions.

The composition of the principal arseniates is contained in the following table :—

Names.	Base.			Acid.	Equiv.	Formulæ.
Tribasic Arseniate of Soda .		93·9	3 eq.	+115·4	1 eq.=209·3	$3Na+AsO_5$.
Do. in crystals with 216 or 24 eq. of water .					. =425·3	
Tribasic Arsen. Soda	Soda	62·6	2 eq.	+115·4	1 eq.=187	$2NaO,HO+AsO_5$
and Basic Water	Water	9	1 eq.			
Do. in crystals with 216 or 24 eq. of water .					. =403	
Do. in crystals with 126 or 14 eq. of water .					. =313	
Acid Arsen. Soda	Soda	31·3	1 eq.	+115·4	1 eq.=164·7	$NaO,2HO+AsO_5$.
and Basic Water	Water	18	2 eq.			
Do. in crystals with 18 or 2 eq. of water .					. =182·7	
Tribasic Arsen. of Potassa .		141·45	3 eq.	+115·4	1 eq.=256·85	$3KO+AsO_5$.
Tribasic Arsen. of Potassa	Potassa	94·3	2 eq.	+115·4	1 eq.=218·7	$2KO,HO+AsO_5$.
and Basic Water	Water	9	1 eq.			
Acid Arsen. of Potas.	Potassa	47·15	1 eq.	+115·4	1 eq.=162·55	$KO,2HO+AsO_5$.
and Basic Water	Water	18	2 eq.			
Triarseniate of Oxide Am.	Ox.Am.	52·30	2 eq.	+115·4	1 eq.=176·7	$2H_4NO,HO+AsO_5$.
and Basic Water	Water	9	1 eq.			
Acid Triarsen. of Ox. Am.	Ox.Am.	26·15	1 eq.	+115·4	1 eq.=159·55	$H_4NO,2HO+AsO_5$.
and Basic Water	Water	18	2 eq.			
Triarseniate of Baryta .		230·1	3 eq.	+115·4	1 eq.=345·5	$3BaO+AsO_5$.
Triarseniate do.	Baryta	153·4	2 eq.	+115·4	1 eq.=277·8	$2BaO,HO+AsO_5$.
with Basic Water	Water	9	1 eq.			
Acid Triarsen. do.	Baryta	76·6	1 eq.	+175·4	1 eq.=211·1	$BaO,2HO+AsO_5$.
with Basic Water	Water	18	2 eq.			
Triarseniate of Lime .		85·5	3 eq.	+115·4	1 eq.=200·9	$3CaO+AsO_5$.
Triarseniate do.	Lime	57	2 eq.	+115·4	1 eq.=181·4	$2CaO,Ho+AsO_5$.
and Basic Water	Water	9	1 eq.			
Acid Triarsen. do.	Lime	28·5	1 eq.	+115·4	1 eq.=161·9	$CaO,2HO+AsO_5$.
and Basic Water	Water	18	2 eq.			
Triarseniate of Ox. Lead .		334·8	3 eq.	+115·4	1 eq.=450·2	$3PbO+AsO_5$.
Triarseniate do.	Lead	223·2	2 eq.	+115·4	1 eq.=347·6	$2PbO,HO+AsO_5$.
and Basic Water	Water	9	1 eq.			
Triarseniate of Ox. Silver .		348	3 eq.	+115·4	1 eq.=463·4	$3AgO+AsO_5$.

Arseniates of Soda.—The triarseniate is made in the same manner as triphosphate of soda, with which it is isomorphous. At 60°, 100 parts of water dissolve 28 of the crystals, and still more by the aid of heat. At 186° they fuse in their water of crystallization.

The triarseniate of soda and basic water corresponds precisely in form and constitution with the corresponding phosphate, and like it parts with its last eq. of water at a red heat; but does not, on losing it, receive any change in its characters. It is efflorescent and alkaline to test paper, and crystallizes best out of an alkaline solution. It is prepared by adding soda or its carbonate in slight excess to a solution of arsenic acid. The salt with 14 eq. of water coincides with the corresponding phosphate.

The acid triarseniate of soda and basic water is prepared like the corresponding phosphate.

The same observation applies to the arseniates of potassa and ammonia, each having its isomorphous arseniate. The triarseniate of potassa crystallizes in needles and with difficulty, like the corresponding triphosphate. The arseniate of potassa may be formed by heating nitre to redness mixed with an equal weight of arsenious acid.

The compound arseniate of potassa and soda agrees in form and composition with the phosphate of those bases.

Arseniates of Baryta.—The triarseniate is best prepared by gradually adding in solution triarseniate of soda to chloride of barium in excess, and falls as a pulverulent heavy precipitate, which is apt to contain a little triarseniate of baryta and basic water as well as the soda salt, and should therefore be well washed with boiling water. On adding chloride of barium to an excess of triarseniate of soda, the latter salt always falls with the precipitate.

To prepare the triarseniate of baryta and basic water a solution of the rhombic triarseniate of soda is added drop by drop to chloride of barium in solution, when the triarseniate soon appears in white crystalline scales, which contain 3 eq. of water. On reversing the process by adding chloride of barium to the arseniate, the precipitate is a mixture of the triarseniate of baryta, and triarseniate of baryta and water. By the continued action of hot water on the latter, it is partly changed into the acid triarseniate and insoluble triarseniate. The acid triarseniate is obtained by dissolving either of the two former salts, in a moist state, by dilute arsenic acid.

Triarseniates of Lime.—The three salts analogous to those of baryta are obtained by precisely similar processes. The triarseniate of lime and basic water occurs in silky acicular crystals as a rare mineral named *pharmacolite*, which contains 5 eq. of water of crystallization.

Triarseniates of Protoxide of Lead.—The triarseniate is formed by adding in solution acetate of oxide of lead gradually to an excess of triarseniate of soda. The same salt falls when acetate of oxide of lead and the rhombic triarseniate of soda are intermixed, acetic acid being set free. It is a white very insoluble powder, which at a low red heat acquires a yellow tint, which it loses again on cooling.

The triarseniate with basic water may be made by a similar process as for forming the corresponding triphosphate, and is a white, insoluble, easily fusible powder.

Triarseniate of Oxide of Silver.—This salt falls as a brick-red powder when nitrate of oxide of silver is mixed in solution with triarseniate of soda or the rhombic triarseniate, in the latter case nitric acid being set free. It is apt to retain some of the nitrate, which cannot be removed by washing; a property which the yellow phosphate of oxide of silver also possesses.

ARSENITES.

These salts have as yet been but little examined. The arsenites of potassa, soda, and ammonia may be prepared by acting with those alkalies on arsenious acid: they are very soluble in water, have an alkaline reaction, and have not been obtained in regular crystals. Most of the other arsenites are insoluble, or sparingly soluble, in pure water; but they are dissolved by an excess of their own acid, with great facility by nitric acid, and by most other acids with which their bases do not form insoluble compounds. The insoluble arsenites are easily formed by double decomposition.

All the arsenites are decomposed when heated in close vessels, the arsenious acid being either dissipated in vapour, or converted, with disengagement of some metallic arsenic, into arseniates. Heated with charcoal or black flux, the acid is reduced with facility. Formiate of soda answers still better.

The soluble arsenites, if quite neutral, are characterized by forming a yellow arsenite of oxide of silver when mixed with the nitrate of that base, and a green arsenite of protoxide of copper, *Scheele's green*, with sulphate of that oxide. When acidulated with acetic or hydrochloric acid, hydrosulphuric acid causes the formation of orpiment. The insoluble arsenites are all decomposed when boiled in a solution of carbonate of potassa or soda.

The arsenite of potassa is the active principle of Fowler's arsenical solution.

CHROMATES.

The salts of chromic acid are mostly either of a yellow or red colour, the latter tint predominating whenever the acid is in excess. The chromates of oxides of the second class of metals are decomposed by a strong red heat, by which the acid is resolved into the green oxide of chromium and oxygen gas; but the chromates of the fixed alkalies sustain a very high temperature without decomposition. They are all decomposed without exception by the united agency of heat and combustible matter. The neutral chromates of protoxides are similar in constitution to the sulphates, being formed of 1 eq. of the base and 1 of chromic acid, the formula being $MO + CrO_3$.

The chromates are in general sufficiently distinguished by their colour. They may be known chemically by the following character:—On boiling a chromate in hydrochloric acid mixed with alcohol, the chromic acid is at first set free, and is then decomposed, a green solution of the chloride of chromium being generated.

The only native chromate hitherto discovered is the red chromate of protoxide of lead from Siberia, in the examination of which Vauquelin made the discovery of chromium.

Chromates of Potassa.—The neutral chromate, from which all the compounds of chromium are directly or indirectly prepared, is made by heating to redness the native oxide of chromium and iron, commonly called *chromate of iron*, with nitrate of potassa, when chromic acid is generated, and unites with the alkali of the nitre. The object to be held in view is to employ so small a proportion of nitre, that the whole of the alkali may combine with chromic acid, and constitute a neutral chromate, which is easily obtained pure by solution in water, and crystallization. For this purpose the chromate of iron is mixed with about a fifth of its weight of nitre, and exposed to a strong heat for a considerable time; and the process is repeated with those portions of the ore which are not attacked in the first operation. It is deposited from its solution in small prismatic anhydrous crystals of a lemon-yellow colour, which, according to Brooke, belong to the right prismatic system.

Chromate of potassa has a cool, bitter, and disagreeable taste. It is soluble to great extent in boiling water, and in twice its weight of that liquid at 60°; but it is insoluble in alcohol. It has an alkaline reaction, and on this account Tassaert* regards it as a subsalt; but Thomson has proved that it is neutral in composition, consisting of 52 parts or 1 eq. of chromic acid, and 47·15 parts or 1 eq. of potassa.†

Bichromate of potassa, which is made in large quantity at Glasgow for dyeing, is prepared by acidulating the neutral chromate with sulphuric, or still better with acetic acid, and allowing the solution to crystallize by spontaneous evaporation. When slowly formed it is deposited in four-sided tabular crystals, the form of which is an oblique rhombic prism. They have an exceedingly rich red colour, are anhydrous, and consist of 1 eq. of the alkali, and 2 eq. of chromic acid. (Thomson.) They are soluble in about ten times their weight of water at 60°, and the solution reddens litmus paper.

The insoluble salts of chromic acid, such as the chromates of baryta and oxides of zinc, lead, mercury, and silver, are prepared by mixing the soluble salts of those bases with a solution of chromate of potassa. The three former are yellow, the fourth orange-red, and the fifth deep red or purple. The yellow chromate of lead, which consists of 1 eq.

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* An. de Ch. et Ph. vol. xxii.

† Annals of Philosophy, vol. xvi.

of acid and 1 eq. of oxide, and is identical with the Siberian red lead ore, the powder of which is pure yellow, is now extensively used as a pigment, and the chromate of oxide of zinc may be used for the same purpose.

A dichromate, composed of 1 eq. of chromic acid and 2 eq. of protoxide of lead, may be formed by boiling the carbonate of that oxide with excess of chromate of potassa. It is of a beautiful red colour, and has been recommended by Badams as a pigment. (An. of Phil. xxv. 303.) It may be also made by boiling the neutral chromate with ammonia or lime-water. Liebig and Wöhler prepare it by fusing nitre at a low red heat, and adding chromate of oxide of lead by degrees until the nitre is nearly exhausted. The chromate of potassa and nitre are then removed by water, and the dichromate is left, crystalline in texture, and of so beautiful a tint that it vies with cinnabar. (Pog. An. xxi. 580.)

Chromates of Silver.—When a soluble salt of chromic acid is added to a solution of nitrate of silver, a deep red-coloured precipitate is obtained, which has usually been considered as the neutral chromate of silver. But it has recently been proved by Warington (Phil. Mag. xi. 489), that if the precipitation be made with acid solutions a bichromate is formed. He also obtained the latter salt by the direct oxidation of metallic silver by a solution of bichromate of potassa acidulated with sulphuric acid. The silver is oxidized at the expense of a part of the chromic acid; while another part, by uniting with the resulting oxide, forms the bichromate, which is deposited in tabular crystals of a rich crimson colour. A chrome alum is at the same time formed, and the oxidation of this silver would appear to be induced by the affinity of the sulphuric acid for the oxide of chromium.

On boiling the bichromate in distilled water, a part is dissolved and separated as the solution cools in beautiful micaceous crystals; but, at the same time, a portion of the salt is decomposed into chromic acid and neutral chromate of silver. As thus formed, the latter is of a dark green colour: it is crimson, however, by transmitted light, and yields by trituration a powder similar in colour to the precipitated chromate.

Bichromate of Chloride of Potassium.—Peligot has described a crystalline compound in which chloride of potassium acts the part of an alkaline base in relation to chromic acid. It is prepared from bichromate of potassa and concentrated hydrochloric acid in the ratio by weight of about 3 to 4, which are to be boiled together for some time in a rather small quantity of water; and it is deposited in flat quadrangular prisms of the same colour as bichromate of potassa.

In this process there is a mutual interchange between the elements of potassa and hydrochloric acid; such that

2 eq. Chromic Acid . .	$2CrO_3$	yield	2 eq. Chromic Acid . .	$2CrO_3$.
1 eq. Potassa . . .	KO		1 eq. Chlo. of Potassium .	KCl.
1 eq. Hydrochloric Acid .	HCl.		1 eq. Water . . .	HO.

For this change to ensue there ought to be a certain excess of hydrochloric acid, and yet not so much as to decompose the chromic acid.

This salt should be dried on bibulous paper. It is permanent in the air. In pure water it is decomposed, the materials from which it was formed, bichromate of potassa and hydrochloric acid, being reproduced; but it may be dissolved without such change in water acidulated by hydrochloric acid. Peligot has made similar bichromates with the chlorides of sodium, calcium, and magnesium, and with hydrochlorate of ammonia, this last salt being exactly similar in appearance to the bichromate of chloride of potassium. (An. de Ch. et Ph. lii. 267.)

BORATES.

As the boracic is a feeble acid, it neutralizes alkalies imperfectly, and hence the borates of soda, potassa, and oxide of ammonium have always an alkaline reaction. For the same reason, when the borates are digested in any of the more powerful acids, such as the sulphuric, nitric, or hydrochloric, the boracic acid is separated from its base. This does not happen, however, at high temperatures; for boracic acid, owing to its fixed nature, decomposes at a red heat all salts, not excepting sulphates, the acid of which is volatile.

The borates of the alkalies are soluble in water, but most of the other salts of this acid are of sparing solubility. They are not decomposed by heat, and the alkaline and earthy borates resist the action of heat and combustible matter. They are remarkably fusible in the fire, a property obviously owing to the great fusibility of boracic acid itself.

The borates are distinguished by the following character:—By digesting any borate in a slight excess of strong sulphuric acid, evaporating to dryness, and boiling the residue in strong alcohol, a solution is formed which has the property of burning with a green flame.

Biborate of Soda.—This salt, the only borate of importance, occurs native in some of the lakes of Thibet and Persia, and is extracted from this source by evaporation. It is imported from India in a crude state, under the name of *Tincal,* which, after being purified, constitutes the *refined borax* of commerce. It is frequently called *sub-borate of soda,* a name suggested by the inconsistent and unphilosophical practice, now quite inadmissible, of regulating the nomenclature of salts merely by their action on vegetable colouring matter. It crystallizes in prisms of the oblique system, which effloresce on exposure to the air, and require twenty parts of cold, and six of boiling water, for solution. When exposed to heat, the crystals are first deprived of their water of crystallization, and then fused, forming a vitreous transparent substance called *glass of borax*. The crystals are composed of 69·8 parts or 2 eq. of boracic acid, 31·3 or 1 eq. of soda, and 90 or 10 eq. of water.

The chief use of borax is as a flux, and for the preparation of boracic acid. Biborate of magnesia is a rare natural production, which is known to mineralogists by the name of *Boracite.*

A new biborate of soda, which contains half as much water of crystallization as the preceding, has been lately described by Buran. It is harder and denser than borax, is not efflorescent, and crystallizes in regular octohedrons. It is made by dissolving borax in boiling water until the sp. gr. of the solution is at 30° or 32° of Beaumé's hydrometer: the solution is then very slowly cooled; and when the temperature descends to about 133°, the new salt is deposited. It is found to be more convenient for the use of jewellers than common borax. (An. de Ch. et Ph. xxxvii. 419.)

The neutral borate of soda has been obtained by Berzelius by the action of boracic acid on carbonate of soda at a boiling heat, when carbonic acid is evolved. The solution on cooling yields crystals of the oblique prismatic system, and containing 8 eq of water. Their constitution is there NaO,BaO_3+8HO. They are powerfully alkaline, and on exposure to the air readily attract carbonic acid, forming the carbonate and biborate of soda. He also obtained the neutral borate of potassa, but was prevented by its great solubility from procuring it in crystals.

CARBONATES.

The carbonates are distinguished from other salts by being decomposed with effervescence, owing to the escape of carbonic acid gas, by nearly all the acids; and all of them, except the carbonates of potassa, soda, and lithia, may be deprived of their acid by heat. The carbonates of baryta and strontia, especially the former, require an intense white heat for decomposition; those of lime and magnesia are reduced to the caustic state by a full red heat; and the other carbonates part with their carbonic acid when heated to dull redness.

All the carbonates, except those of potassa, soda, and ammonia, are of sparing solubility in pure water; but all of them are more or less soluble in an excess of carbonic acid, owing doubtless to the formation of supersalts.

Several of the carbonates occur native, among which may be enumerated the carbonates of soda, baryta, strontia, lime, magnesia, and of the protoxides of manganese, iron, copper, and lead; together with some double carbonates, such as dolomite or the double carbonate of lime and magnesia, and baryto-calcite or the double carbonate of baryta and lime.

The composition of the principal carbonates is stated in the following table:—

Names.	Base.	Acid.	Equiv.	Formulæ.
Carbonate of Potassa . .	47·15 1 eq.	+22·12 1 eq.	= 69·27	$KO+CO_2$.
Bicarbonate do. . . .	47·15 1 eq.	+44·24 2 eq.	= 91·39	$KO+2CO_2$.
Do. in crystals with	9 or 1 eq. of water . .		=100·39	
Carbonate of Soda . . .	31·3 1 eq.	+22·12 1 eq.	= 53·42	$NaO+CO_2$.
Do. in crystals with	90 or 10 eq. of water . .		=143·42	
Do.	63 or 7 eq. of water . .		=116·42	
Bicarbonate of Soda . .	31·3 1 eq.	+44·24 2 eq.	= 75·54	$NaO+2CO_2$.
Do. in crystals with	9 or 1 eq. of water . .		= 84·54	
Carbonate of Ammonia .	17·15 1 eq.	+22·12 1 eq.	= 39·27	H_3N+CO_2.
Bicarbonate ditto . .	17·15 1 eq.	+44·24 2 eq.	= 61·39	$H_4NO+2CO_2$.
Carbonate of Baryta . .	76·7 1 eq.	+22·12 1 eq.	= 98·82	$BaO+CO_2$.
———— Strontia . .	51·8 1 eq.	+22·12 1 eq.	= 73·92	$SrO+CO_2$.
———— Lime . .	28·5 1 eq.	+22·12 1 eq.	= 50·62	$CaO+CO_2$.
———— Magnesia .	20·7 1 eq.	+22·12 1 eq.	= 42·82	$MgO+CO_2$.
———— Do. in crystals with	27 or 3 eq. of water		= 69·82	
Carbonate Protox. of Iron	36 1 eq.	+22·12 1 eq.	= 58·12	$FeO+CO_2$.
Dicarbonate Protox. Copper	79·2 1 eq.	+22·12 1 eq.	=101·32	$2CuO+CO_2$.
Do. in malachite with	9 or 1 eq. of water . .		=110·32	
Carbonate Protox. Lead	111·6 1 eq.	+22·12 1 eq.	=133·72	
Dicarbon. Perox. Mercury	436 2 eq.	+22·12 1 eq.	=458·12	$2HgO+CO_2$.

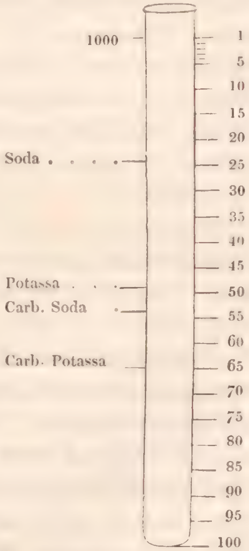
Double Carbonates.

Carbonate of Lime and Magnesia	Carb. Lime . .	50·62	1 eq.	= 93·44	MgO,CO_2+CaO,CO_2.
	Carb. Magnesia .	42·82	1 eq.		
Carbon. of Baryta and Lime	Carb. Baryta .	98·82	1 eq.	=149·44	CaO,CO_2+BaO,CO_2.
	Carb. Lime .	50·62	1 eq.		

Carbonate of Potassa.—This salt is procured in an impure form by burning land plants, lixiviating their ashes, and evaporating the solution to dryness; a process which is performed on a large scale in Russia and America. The carbonate, thus obtained, is known in commerce by the names of *potash* and *pearlash*, and is much employed in the arts, especially in the formation of soap and the manufacture of glass. When derived from this source it always contains other compounds, such as sulphate of potassa and chloride of potassium; and therefore, for chemical purposes, it should be prepared from cream of tartar. On heating this salt to redness the tartaric acid is decomposed, and a pure carbonate of potassa mixed with charcoal remains. The carbonate is then dissolved in water, and, after filtration, is evaporated to dryness in a capsule of platinum or silver.

Pure carbonate of potassa has a taste strongly alkaline, is slightly caustic, and communicates a green tint to the blue colour of the violet. It dissolves in less than an equal weight of water at 60°, deliquesces rapidly on exposure to the air, and crystallizes with much difficulty from its solution. In pure alcohol it is insoluble. It fuses at a full red heat, but undergoes no other change.

It is often necessary, for commercial purposes, to ascertain the value of different samples of pearlash; that is, to determine the quantity of real carbonate of potassa contained in a given weight of impure carbonate. A convenient mode of effecting this object is described by Faraday in his excellent work on *Chemical Manipulation.* Into a tube sealed at one end, 9½ inches long, ¾ of an inch in diameter, and as cylindrical as possible in its whole length, pour 1000 grains of water, and with a file or diamond mark the place where its surface reaches, and divide the space occupied by the water into 100 equal parts, as is shown in the annexed woodcut. Opposite to the numbers 23·44, 58·96, 54·63, and 65, draw a line, and at the first write soda, at the second potassa, at the third carbonate of soda, and at the fourth carbonate of potassa. Then prepare a dilute acid having the specific gravity of 1·127 at 60°, which may be made by mixing one measure of concentrated sulphuric acid with four measures of distilled water. This is the standard acid to be used in all the experiments, being of such strength that when poured into the tube till it reaches either of the four marks just mentioned, we shall obtain the exact quantity necessary for neutralizing 100 grains of the alkali written opposite to it. If, when the acid reaches the word *carb. potassa*, and when, consequently, we have the exact quantity which will neutralize 100 grains of that carbonate, pure water be added until it reaches 1, or the beginning of the scale, each division of this mixture will neutralize one grain of carbonate of potassa. All that is now required, in order to ascertain the quantity of real carbonate in any specimen of pearlash, is to dissolve 100 grains of the sample in warm water, filter to remove all the insoluble parts, and add the dilute acid in successive small quantities, until by the test of litmus paper, the solution is exactly neutralized. Each division of the mixed acid employed indicates a grain of pure carbonate.



It is convenient, in conducting this process, to set aside a portion of the alkaline liquid, in order to neutralize the acid, in case it should at first be added too freely. To this instrument the term *alkalimeter* is given, a name obviously derived from the use to which it is applied.

Bicarbonate of Potassa is made by transmitting a current of carbonic acid gas through a solution of the carbonate; or by evaporating a mixture of the carbonates of ammonia and potassa, the ammonia being dissipated in a pure state. By slow evaporation the bicarbonate is deposited from the liquid in hydrated prisms with eight sides, terminated with dihedral summits.

Bicarbonate of potassa, though far milder than the carbonate, is alkaline both to the taste and to test paper. It does not deliquesce on exposure to the air. It requires four times its weight of water at 60° for solution, and is much more soluble at 212°; at this temperature it has been stated to be converted into sesquicarbonate, but H. Rose has shown that, though gradually, it at length parts with half its carbonic acid. The escape of the gas he finds to be much retarded by pressure, that of one inch of mercury making a difference; hence the loss of carbonic acid is much more rapid when a cold solution is evaporated in vacuo, both the gas and aqueous vapour being absorbed by quicklime. (Pog. An. xxxiv. 149.) At a low red heat it is converted into the carbonate.

Thomson, in his "First Principles," has described a sesquicarbonate which was discovered by Nimmo of Glasgow. Its crystals contain 12 eq. of water, as denoted by the formula $2KO,3CO_2 + 12HO$.

Carbonate of Soda.—The carbonate of commerce is obtained by lixiviating the ashes of sea-weeds. The best variety is known by the the name of *barilla*, and is derived chiefly from the *salsola soda* and *salicornia herbacea.* A very inferior kind, known by the name of *kelp*, is prepared from sea-weeds on the northern shores of Scotland. The purest barilla, however, though well fitted for making soap and glass, and for other purposes in the arts, always contains the sulphates of potassa and soda, and the chlorides of potassium and sodium. A purer carbonate is prepared by heating a mixture of sulphate of soda, made from sea-salt, saw-dust, and lime, in a reverberatory furnace. By the action of carbonaceous matter, the sulphuric acid is decomposed; its sulphur partly uniting with calcium and partly being dissipated in the form of sulphurous acid, while the carbonic acid, which is generated during the process, unites with soda. The carbonate of soda is then obtained by lixiviation and crystallization. It is difficult to obtain this salt quite free from sulphuric acid.

It crystallizes in rhombic octohedrons, the acute angles and edges of which are generally truncated. The crystals effloresce on exposure to the air, and, when heated, dissolve in their water of crystallization. By continued heat they are rendered anhydrous without loss of carbonic acid. They dissolve in about two parts of cold, and in rather less than their weight of boiling water, and the solution has a strong alkaline taste and reaction. The crystals commonly found in commerce contain 10 eq. of water; but when formed at a temperature of about 80°, they retain only 7 eq.

The purity of different specimens of barilla, or other carbonates of soda, may be ascertained by means of the alkalimeter just described.

Bicarbonate of Soda.—This salt is made by the same processes as bicarbonate of potassa, and is deposited in hydrated crystalline grains by evaporation. Though still alkaline, it is much milder than the carbonate, and far less soluble, requiring about ten times its weight of water at 60° for solution. It is found by Rose to undergo the same changes on boiling as the bicarbonate of potassa; it is converted into the carbonate by a red heat.

Sesquicarbonate.—This compound occurs native on the banks of the lakes of soda in the province of Sukena in Africa, whence it is exported under the name of *Trona*. It was first distinguished from the two other carbonates by Phillips (Journal of Science, vii.), whose analysis corresponds with that of Klaproth. Its formula is $2NaO,3CO_2 + 4HO$.

Carbonate of Ammonia.—The only method of obtaining the substance so called is by mixing perfectly dry carbonic acid and ammoniacal gases. In whatever proportion the two gases be mixed, they unite only in the ratio of one volume of the former to two of the latter, and condense into a white light powder. This substance therefore contains carbonic acid and ammonia in equivalent proportions, but it is probable that the elements are not arranged as expressed by the name. By the action of water it is instantly decomposed into ammonia and the sesquicarbonate.

Bicarbonote of Oxide of Ammonium.—This salt was formed by Berthollet by transmitting a current of carbonic acid gas through a solution of the common carbonate of ammonia of the shops. On evaporating the liquid by a gentle heat, the bicarbonate is deposited in small prisms of the right rhombic system, which have no smell, and very little taste. Berthollet ascertained that it contains twice as much acid as the carbonate. It cannot exist without the presence of water, of which it contains 22·7 per cent. (Berzelius), or 2 eq. It may therefore be considered as carbonate of basic water and carbonate of oxide of ammonium, or $HO,CO_2 + H_4NO,CO_2$.

Sesquicarbonate of Oxide of Ammonium.—The common carbonate of ammonia of the shops, *sub-carbonas ammoniæ* of the pharmacopœia, is different from both these compounds. It is prepared by heating a mixture of one part of hydrochlorate of ammonia with one part and a half of carbonate of lime, carefully dried. Double decomposition ensues during the process: chloride of calcium remains in the retort, and hydrated sesquicarbonate of ammonia is sublimed. The carbonic acid and ammonia are, indeed, in proper proportion in the mixture for forming the real carbonate; but, owing to the presence of water generated by the combination of the oxygen of the lime with the hydrogen of the hydrochloric acid, part of the ammonia is disengaged in a free state.

The salt thus formed consists, according to the analysis of Phillips, Ure, and Thomson, of 34·3 parts or 2 eq. of ammonia, 66·36 parts or 3 eq. of carbonic acid, and 18 parts or 2 eq. of water. It is therefore anhydrous sesquicarbonate of oxide of ammonium, or $2H_4NO + 3CO_2$. When recently prepared, it is hard, compact, translucent, of a crystalline texture, and pungent ammoniacal odour; but if exposed to the air, it loses weight rapidly from the escape of pure ammonia, and becomes an opaque brittle mass, which is the bicarbonate. The results obtained by Rose, who has lately studied the carbonates of ammonia with care, will be given in the organic chemistry, where ammonia, as containing a compound radical, is more properly placed.

Carbonite of Baryta occurs abundantly in the lead mines of the north of England, where it was discovered by Dr. Withering, and has hence received the name of *Witherite.* It may be prepared by way of double decomposition, by mixing a soluble salt of baryta with any of the alkaline carbonates or bicarbonates. It is anhydrous, exceedingly insoluble in distilled water, requiring 4300 times its weight of water at 60°, and 2300 of boiling water for solution; but when recently precipitated, it is dissolved much more freely by a solution of carbonic acid. It is highly poisonous.

Carbonate of Strontia, which occurs native at Strontian in Argyleshire, and is known by the name of *Strontianite*, may be prepared in the same manner as carbonate of baryta. It is anhydrous, and very insoluble in pure water, but is dissolved by an excess of carbonic acid.

Carbonate of Lime.—This salt is a very abundant natural production, and occurs under a great variety of forms, such as common limestone, chalk, marble, and Iceland spar, and in regular anhydrous crystals, the density of which is 2·7. It may also be formed by precipitation. Though sparingly soluble in water, it is dissolved by carbonic acid in excess; and hence the spring-water of limestone districts always contains carbonate of lime, which is deposited when the water is boiled.

Daniell noticed that an aqueous solution of sugar and lime deposited crystallized carbonate of lime by exposure to the air. Gay-Lussac has proved that the sugar merely acts as a solvent, presenting lime in a favourable state for combining with the carbonic acid of the atmosphere; and that all the lime is deposited in acute rhombohedrons, which contain 5 eq. of water to 1 eq. of carbonate of lime. These crystals are insoluble and remain unchanged in cold water; but in water at 86°, or in air, they lose their combined water, and fall to powder. When boiled in alcohol they retain their form, but lose 2 eq. of water, and retain 3 eq. in combination. (An. de Ch. et Ph. xlviii. 301.)

Carbonate of Magnesia.—It is met with occasionally in rhombohedral crystals, and in a pulverulent earthy state, but more commonly as a compact mineral of an earthy fracture called *Magnesite.* A specimen of magnesite from the East Indies, where, I am informed, it is abundant, has been analyzed by Henry, who found it to be nearly pure anhydrous carbonate of magnesia: it is of a snow-white colour, of density 2·56, and so hard that it strikes fire with steel. (An. of Phil. xvii. 252.) It is obtained in minute transparent hexagonal prisms with 3 eq. of water, when a solution of bicarbonate of magnesia evaporates spontaneously in an open vessel. The crystals lose their water and become opaque by a very gentle heat, and even in a dry air at 60°. By cold water they are decomposed, yielding a soluble bicarbonate and an insoluble white compound of hydrate and carbonate of magnesia; and hot water produces the same change with disengagement of carbonic acid, without dissolving any magnesia. The formula of the crystals is $MgO,CO_2 + 3HO$. (Berzelius.) Fritzsche obtained in the same way, besides the salt of Berzelius, another in tabular crystals, containing 5 eq. water, $MgO,CO_2 + 5HO$. When heated, it loses carbonic acid, and leaves a new compound, $4(MgO,CO_2) + MgO,5HO$.

When carbonate of potassa is added in excess to a hot solution of sulphate of magnesia, a white precipitate falls, which after being well washed has been long considered as pure carbonate of magnesia; but Berzelius has shewn that it consists of the following ingredients:—

Magnesia .	44·75	82·8 or 4 eq.	Probable formula is
Carbonic Acid .	35·77	66·36 or 3 eq.	
Water . .	19·48	36 or 4 eq.	$MgO,4HO+3MgO,CO_2$.
	100·00	185·16 or 1 eq.	

This compound is said to require 2493 parts of cold, and 9000 of hot water for solution. It is freely dissolved by a solution of carbonic acid, bicarbonate of magnesia being generated; but on allowing the solution to evaporate spontaneously, carbonic acid is given off, and crystals of the hydrated carbonate above mentioned are obtained.

Carbonate of Protoxide of Iron.—Carbonic acid does not form a definite compound with peroxide of iron, but with the protoxide it constitutes a salt which is an abundant natural production, occurring sometimes massive, and at other times crystallized in rhombohedrons. This protocarbonate is contained also in most of the chalybeate mineral waters, being held in solution by free carbonic acid; and it may be formed by mixing an alkaline carbonate with the sulphate of protoxide of iron. When prepared by precipitation it attracts oxygen rapidly from the atmosphere, and the protoxide of iron, passing into the state of peroxide, parts with carbonic acid. For this reason, the carbonate of iron of the pharmacopœia is of a red colour, and consists chiefly of the peroxide.

Dicarbonate of Protoxide of Copper.—It occurs as a hydrate in the beautiful green mineral called *malachite;* and the same compound, as a green powder, the *mineral green* of painters, may be obtained by precipitation from a hot solution of sulphate of protoxide of copper by carbonate of soda or potassa. When obtained from a cold solution, it falls as a bulky hydrate of a greenish-blue colour, which contains more water than the green precipitate. By careful drying its water may be expelled. When the hydrate is boiled for a long time in water, it loses both carbonic acid and combined water, and the colour changes to brown. The rust of copper, prepared by exposing metallic copper to air and moisture, is a hydrated dicarbonate.

The blue-coloured mineral, called *blue copper ore,* appears to be a hydrate and carbonate of the protoxide of copper, and consists, according to the analysis of Phillips, of (Quarterly Journal of Science, v.)

Protoxide of Copper	69·08	118 or 3 eq.	Probable formula is
Carbonic Acid .	25·46	44·24 2 eq.	
Water . .	5·46	9 1 eq.	$CuO,HO+2CuO,CuO_2$.
	100·00	171·24 1 eq.	

The blue pigment called *verditter*, prepared by decomposing nitrate of oxide of copper with chalk, has a similar composition. (Phillips.)

Carbonate of Protoxide of Lead.—This salt, which is the *white lead*, or *ceruse* of painters, occurs native in white prismatic crystals derived from a right rhombic prism, the sp. gravity of which is 6·72. It is obtained as a white pulverulent precipitate by mixing solutions of an alkaline carbonate with acetate of protoxide of lead; and it is prepared as an article of commerce from the subacetate by a current of carbonic acid, by exposing metallic lead in minute division to air and moisture, and by the action on thin sheets of lead of the vapour of vinegar, by which the metal is both oxidized and converted into a carbonate.

Dicarbonate of Peroxide of Mercury.—When a solution of the nitrate of peroxide of mercury is decomposed by carbonate of soda, an ochre-yellow precipitate falls, which Phillips finds to be a dicarbonate. The protoxide appears to form no compound with carbonic acid; for when a nitrate of that oxide is decomposed by any alkaline carbonate, the precipitate is either black at first, or speedily becomes so, and after being washed is quite free from carbonic acid.

Double Carbonates.—One of the most remarkable of these is the double carbonate of lime and magnesia, which constitutes the minerals called bitter-spar, pearl-spar, and dolomite. The two former occur in rhombohedrons of nearly the same dimensions as carbonate of lime. The latter is met with in great perfection in the Alps, and there usually occurs in white masses of a granular texture; the grains often cohere loosely, but other specimens are hard and compact, and when broken present the crystalline aspect of marble. Its density is 2·884. Some specimens consist of the two constituent carbonates in the ratio of their eq., as stated in the table; but the ratio of the ingredients, as may be expected, is very variable, since isomorphous substances crystallize together in all proportions. Carbonate of protoxide of manganese is often associated with them. The rock called *magnesian limestone* may be viewed as an impure earthy variety of dolomite.

The double carbonate of baryta and lime constitutes the mineral called *baryto-calcite*, which Mr. Children found to contain the two carbonates in atomic proportion.

Berthier has made some interesting experiments on the production of double carbonates by fusion. Carbonate of soda, when fused with carbonate of baryta, strontia, or lime, in the ratio of their eq., yields uniform crystalline compounds, which have all the appearance of being definite. An eq. of dolomite fuses in like manner with 4 eq. of carbonate of soda. Five parts of carbonate of potassa and four of carbonate of soda, corresponding to an eq. of each, fuse with remarkable facility; and this mixture, by reason of its fusibility, may be advantageously employed in the analysis of earthy minerals.

Compounds similar to the foregoing may be generated by heating sulphate of soda with carbonate of baryta, strontia, or lime, in the ratio of their eq.; or by employing the sulphate of these bases and carbonate of soda. In like manner carbonate of soda fuses with chloride of barium or calcium; and chloride of sodium with carbonate of baryta or lime. (An. de Ch. et Ph. xxxviii.)

SECTION II.

CLASS OF SALTS. ORDER II.

HYDRO-SALTS.

In this section are included those salts only, the acid or base of which is a compound containing hydrogen as one of its elements. For reasons already assigned I have already described all those salts which were formerly called *muriates* or *hydrochlorates* of metallic oxides as chlorides of metals, considering that in general the neutralizing power of hydrochloric acid is not due to its direct combination with an oxide, but to chlorine uniting with the metal itself. The same remark applies to the hydriodic and other hydracids, the salts of which are consequently reduced to a small number. The only salts, indeed, which are included in this section, are compounds of the hydracids with ammonia and phosphuretted hydrogen. Some of the compounds which might, as containing an hydracid, be comprehended in this section, may with greater propriety be placed in the fourth, seeing that in them the hydracid acts rather as a base or electro-positive ingredient than as an acid or electro-negative substance. This double function, which chemists have long recognized in certain metallic oxides, such as alumina and oxide of zinc, appears to be performed even by so powerful an acid as the hydrochloric. Some judicious observations on this subject have been made by Professor Kane of Dublin. (Dublin Journal of Science, i. 265.)

The compounds of ammonia with the hydracids may be described as compounds of the hypothetical radical ammonium with the radicals of the hydracids. The argument for doing so is derived from the similarity of the hydrochlorate of ammonia, for example, to the chloride of potassium in its crystalline form, and all its relations to other chlorides. But the argument does not apply with equal force in both cases; for, to suppose a direct compound of ammonia and an hydracid is perfectly consistent with observation, whereas the existence of a compound of ammonia and an ox-acid is directly opposed to it. In the former case, therefore, we have two ways of accounting for the phenomena observed; in the latter we have but one, and that one, therefore, though hypothetical, must be adopted. As this necessity does not exist in the compounds of ammonia with the hydracids, they are treated as direct binary combinations of their constituents; but it must not be forgotten that both views are admissible, and are indeed adopted by different chemists.

Ammonia unites with fluoride of boron, bisulphuret of carbon, and some other bi-elementary compounds, which contain neither oxygen nor hydrogen, constituting saline combinations, which are included in this section, and to which, considering the distinct alkaline character of ammonia, the ordinary nomenclature of salts is applicable.

AMMONIACAL SALTS.

These compounds are readily recognized by the addition of pure potassa or lime, when the odour of ammonia may be perceived. Those which contain a volatile acid may in general be sublimed without decomposition; but the ammonia is expelled by heat from those acids which are much more fixed than itself. The most important of these salts are thus constituted:—

Names.	Base.	Acid.	Equiv.	Formulæ.
Hydrochlorate of Ammonia	17·15	1 eq.+ 36·42	1 eq.= 53·57	H_3N+HCl or NH_4,Cl.
Hydriodate do. .	17·15	1 eq.+127·3	1 eq.=144·45	H_3N+HI or NH_4,I.
Hydrobromate do.	17·15	1 eq.+ 79·4	1 eq.= 96·55	H_3N+HBr or NH_4,Br.
Hydrofluate do.	17·15	1 eq.+ 19·68	1 eq.= 36·83	H_3N+HF or NH_4,F.
Hydrosulphate do.	17·15	1 eq.+ 17.1	1 eq.= 34·25	H_3N+HS or NH_4,S.
Trifluoborate do.	51·45	3 eq.+ 66·94	1 eq.=118·39	$3H\ N+BF_3$.
Difluoborate do. .	34·30	2 eq.+ 66·94	1 eq.=101·24	$2H_3N+BF_3$.
Fluoborate do. .	17·15	1 eq.+ 66·94	1 eq.= 84·09	H_3N+BF_3.
Fluosilicate do. .	17·15	1 eq.+ 78·54	1 eq.= 95·69	H_3N+SiF_3.
Carbosulphate do.	17·15	1 eq.+ 38·32	1 eq.= 55·47	H_3N+CS_2.

Hydrochlorate of Ammonia.—This salt, *sal-ammoniac* of commerce, was formerly imported from Egypt, where it is procured by sublimation from the soot of camel's dung; but it is now manufactured in Europe by several processes. The most usual is to decompose sulphate of ammonia by the chloride either of sodium or magnesium, when double decomposition ensues, giving rise in both cases to hydrochlorate of ammonia, and to sulphate of soda when chloride of sodium is used, and to sulphate of magnesia when chloride of magnesium is employed. The sal-ammoniac is afterwards obtained in a pure state by sublimation. The method now generally used in this country for obtaining sulphate of oxide of ammonium is, to decompose with sulphuric acid the hydrosulphate and hydrocyanate of ammonia which is collected in the manufacture of coal-gas; but it may also be procured either by lixiviating the soot of coal, which contains sulphate of oxide of ammonium in considerable quantity, or by digesting with gypsum impure sesquicarbonate of oxide of ammonium, procured from the destructive distillation of bones and other animal substances, so as to form an insoluble carbonate of lime and a soluble sulphate of oxide of ammonium.

Hydrochlorate of ammonia has a pungent saline taste, a density of 1·45, and is tough and difficult to be pulverized. It is soluble in alcohol and water, requiring for solution three times its weight of water at 60°, and an equal weight at 212°. It usually crystallizes from its solution in feathery crystals, but sometimes in cubes or octohedrons. At a temperature below that of ignition it sublimes without fusion or decomposition, and condenses on cool surfaces as an anhydrous salt, which absorbs humidity in a damp atmosphere, but is not deliquescent. It is generated by the direct union of hydrochloric and ammoniacal gases, which unite in equal volumes.

Its eq. is 53.5 ; symb. $NH_3 + HCl$ or NH_4,Cl.

Hydriodate of Ammonia.—It is formed as a white powder by the direct union in equal measures of hydriodic and ammoniacal gases, or by neutralizing a solution of hydriodic acid with ammonia, and evaporating. It crystallizes with difficulty in anhydrous cubes, is very soluble in water, and deliquesces in a moist atmosphere. In close vessels it may be sublimed without change ; but it suffers partial decomposition when heated in the open air.

When a concentrated solution of this salt is digested with iodine, a brown solution is obtained, the nature of which is not understood.

Hydrobromate of Ammonia is a white anhydrous salt, which may be formed by similar processes as the hydriodate. It is soluble in water, and crystallizes by evaporation in quadrilateral prisms.

Hydrofluate of Ammonia.—It is prepared by mixing one part of sal-ammoniac with 2¼ of fluoride of sodium, both dry and in fine powder, gently heating the mixture in a platinum vessel, and receiving the sublimed salt in a second platinum vessel, the temperature of which is not allowed to exceed 212°. Chloride of sodium is generated, and hydrofluate of ammonia is obtained in small anhydrous prismatic crystals, which may be preserved unchanged in the air, is partly soluble in alcohol, and dissolves readily in water. At an elevated temperature it fuses before subliming. It acts powerfully on glass even in its dry state.

When this salt is introduced in a dry state into ammoniacal gas, absorption ensues, and the resulting salt appears to be a dihydrofluate of ammonia. By sublimation it loses ammonia and becomes neutral. An acid salt, apparently a bi-hydrofluate, is obtained by evaporating the aqueous solution of the neutral hydrofluate, ammonia being disengaged. If the evaporation take place at 100°, it separates in crystalline grains, which reddens litmus, and deliquesces rapidly at common temperatures.

Hydrosulphate of Ammonia.—This salt, also called hydrosulphuret of ammonia, and formerly the *Fuming Liquor of Boyle*, is prepared by heating a mixture of one part of sulphur, two of sal-ammoniac, and two of unslaked lime. The changes which ensue have been explained by Gay-Lussac. The volatile products are ammonia and hydrosulphate of ammonia; and the fixed residue consists of sulphate of lime with chloride and sulphuret of calcium. The hydrosulphuric acid is formed from the hydrogen of hydrochloric acid uniting with sulphur, and the oxygen of the sulphuric acid is derived from decomposed lime, the calcium of which is divided between the chlorine of the hydrochloric acid and sulphur. Hydrosulphate of ammonia may also be formed by the direct union of its constituent gases, and if they are mixed in a glass globe kept cool by ice, the salt is deposited in crystals. It is much used as a reagent, and for this purpose is usually prepared by saturating a solution of ammonia with hydrosulphuric acid gas, or by precipitating sulphuret of barium with carbonate of ammonia. A mixture of sulphuret of barium, water, and sal-ammoniac, when distilled, also yields this compound. It is frequently called, by the Continental chemists, sulphuret of ammonium, and has all the characters of a sulphuret.

The neutral compound, the formula of which is NH_3,HS, or NH_4,S, is colourless; but there are several compounds, which, according to Fritzsche, are formed by the addition of an excess of sulphur to it, and which are all more or less yellow and orange. These compounds exactly correspond to the supersulphurets of potassium, and have the formulæ NH_4,S_2; NH_4,S_3; NH_4,S_5. Their existence and properties are strong arguments in favour of the view which regards the neutral compound as sulphuret of ammonium. On the other view, these bodies must either be compounds of the neutral salt with sulphur,—a most unlikely combination,—or compounds of 2, 3, and 5 eqs. of sulphuretted hydrogen, with 1 eq. of ammonia, which does not agree with the amount of hydrogen they contain. Fritzsche has lately described some more sulphurets of ammonium.

When the solution of the neutral compound is exposed to the air it becomes yellow, owing to the formation of persulphuret, ammonia being at the same time set free, and oxygen absorbed from the atmosphere. $2(NH_4,S) + O = NH_4,S_2 + HO + NH_3$.

Liebig has given the following method of preparing the neutral sulphuret of ammonium in solution:—two equal portions of aqua ammoniæ are taken, and one of them saturated with hydrosulphuric acid. By this means there is formed a compound of sulphuret of ammonium as a sulphur base with hydrosulphuric acid as a sulphur acid, $NH_3 + 2HS = NH_4,S + HS$. The other portion of ammonia is now added, and the result is pure protosulphuret of ammonium. $(NH_4,S + HS) + NH_3 = 2(NH_4,S)$.

Fluoborates of Ammonia.—Fluoboric acid combines with three times and with twice its volume of ammoniacal gas, forming a trifluoborate and difluoborate, which are liquid at common temperatures. The neutral fluoborate is formed of equal volumes of its constituent gases, and is a white volatile salt, soluble in water, but which cannot be recovered from the solution; for on evaporation, a subfluoborate of ammonia is expelled, and boracic acid is left in solution. The neutral fluoborate is formed by heating gently either of the subfluoborates.

Fluosilicate of Ammonia.—Fluosilicic acid and ammoniacal gases unite by volume in the ratio of 1 to 2, forming a white volatile salt which is decomposed by water.

Carbosulphate of Ammonia.—When dry ammoniacal gas is brought into contact with bisulphuret of carbon, direct combination ensues, and there results an uncrystalline solid mass of a straw-yellow colour, which may be sublimed without decomposition. By contact with water, or exposure to a moist air, an interchange ensues between the elements of water and bisulphuret of carbon, giving rise to hydrosulphuric and carbonic acids; and a sulphur-salt of an orange-yellow colour, the hydrocarbosulphuret of ammonia, is generated.

Arsenio-persulphate of Ammonia.—Berzelius states that when dry persulphuret of arsenic is exposed to ammoniacal gas, absorption ensues, and a yellowish white compound results; but the elements are united by a feeble attraction, and on mere exposure to the air the ammonia escapes.

SALTS OF PHOSPHURETTED HYDROGEN.

Rose has lately called the attention of chemists to the close analogy which exists in the composition of ammonia and phosphuretted hydrogen, and in some of their properties. The latter is a feeble alkaline base, which combines with some of the hydracids. The salt best known is the hydriodate of phosphuretted hydrogen, first noticed by Gay-Lussac, which it formed of 137·3 parts or 1 eq. of acid and 31·4 parts or 1 eq. of base, and crystallizes in cubes. The crystals are permanent while quite dry; but with water, or the moisture of the air, they yield a solution of hydriodic acid, and phosphurretted hydrogen gas escapes. These salts are all decomposed by water, and exist only in the anhydrous state.

SECTION III.

CLASS OF SALTS. ORDER III.

SULPHUR-SALTS.

The compounds described in this section are double sulphurets, just as the oxy-salts in general are double oxides. Their resemblance in composition to salts is perfect. The principal *sulphur-bases* are the protosulphurets of potassium, sodium, lithium, barium, strontium, calcium, and magnesium, and hydro-sulphate of ammonia, (sulphuret of ammonium); and the principal *sulphur-acids* are the sulphurets of arsenic, antimony, tungsten, molybdenum, tellurium, tin and gold, together with hydrosulphuric acid, bisulphuret of carbon, and sulphuret of selenium. The sulphur-salts with two metals are so constituted, that if the sulphur in each were replaced by an eq. quantity of of oxygen, an oxy-salt would result. The analogy between oxy-salts and sulphur-salts is rendered still closer by the circumstance that hydrosulphuric and hydrosulphocyanic acids have the characteristic properties of acidity, and unite both with ammonia and with sulphur-bases.

The sulphur-salts may be divided into families, characterized by containing the same sulphur-acid. For the purpose of indicating that such salts are double sulphurets, as well as to distinguish them readily from other kinds of salts, I shall construct the generic name of each family from the sulphur acid terminated with sulphuret. Thus the salts which contain persulphuret of arsenic or hydrosulphuric acid as the sulphur-acid are termed *arsenio-sulphurets* and *hydro-sulphurets;* and a salt composed of each of these sulphur-acids with sulphuret of potassium is termed *arsenio-sulphuret* and *hydro-sulphuret* of sulphuret of potassium. For the sake of brevity the metal of the base may alone be expressed, it being understood that the positive metal in a sulphur-salt enters as a protosulphuret into the compound.

HYDRO-SULPHURETS.

The sulphur-salts contained in this group have hydrosulphuric acid for their electro-negative ingredient. Most of them which have been studied are soluble in water, and may be obtained in crystals by evaporation. They are decomposed by exposure to the air, yielding at first bisulphurets of the metal, and then a hyposulphite. By acids the hydrosulphuric acid is expelled with effervescence. They are thus constituted:—

Name.		Sulphur-base.	Sulphur-acid.	Equiv.	Formulæ.
Hydro-sulphuret of	Potassium	55·25	1 eq.+17·1	1 eq.=72·35	$KS+HS$.
Ditto	Sodium .	40·4	1 eq.+17·1	1 eq.=57·5	$NaS+HS$.
Ditto	Lithium .	26·1	1 eq.+17·1	1 eq.=43·2	$LS+HS$.
Ditto	Barium .	84·8	1 eq.+17·1	1 eq.=10·19	$BaS+HS$.
Ditto	Strontium	59·9	1 eq.+17·1	1 eq.=77·0	$SrS+HS$.
Ditto	Calcium .	36·6	1 eq.+17·1	1 eq.=53·7	$CaS+HS$.
Ditto	Magnesium	28·8	1 eq.+17·1	1 eq.=45·9	$MgS+HS$.

Hydro-sulphuret of Potassium.—This salt is obtained in the anhydrous state by introducing anhydrous carbonate of potassa into a tubulated retort, transmitting through it a current of hydrosulphuric acid gas, and heating the salt to low redness. The mass becomes black, fuses, and boils from the escape of carbonic acid gas and aqueous vapour; and after the ebullition has ceased, the gas is continued to be transmitted until the retort is quite cold. The resulting anhydrous hydro-sulphuret of potassium, though black while in fusion, is white when cold, and of a crystalline texture; but if air has not been perfectly excluded, it has a yellow tint, owing to the presence of some bisulphuret of potassium.

The same salt is prepared in the moist way by introducing a solution of pure potassa, free from carbonic acid, into a tubulated retort, expelling atmospheric air by a current of hydrogen gas, and then saturating the solution with hydrosulphuric acid. At first, the potassa, as in the former process, interchanges elements with the gas, yielding water and protosulphuret of potassium; after which the protosulphuret unites with hydrosulphuric acid. The solution should be evaporated in the retort to the consistence of syrup, a current of hydrogen gas being transmitted through the apparatus the whole time; and on cooling the salt crystallizes in large four or six-sided prisms, which are colourless if air was perfectly excluded. The crystals contain water of crystallization, have an acrid, alkaline, and bitter taste, deliquesce in open vessels, and dissolve freely in water and alcohol. On exposure to the air it acquires a yellow colour, from the formation of bisulphuret of potassium.

Hydro-sulphuret of Sodium.—It is prepared on the same principles as the former salt, and yields by evaporation colourless crystals. When a hot concentrated solution is mixed with a solution of hydrate of soda also concentrated, the mixture on cooling deposits four-sided prisms, which are protosulphuret of sodium with water of crystallization. The interchange of elements is such that

1 eq. Hydro-sulphuret	and 1 eq. Soda	yield	2 eq. Sulphuret	and 1 eq. water.
$NaS+HS$	NaO		$2NaS$	HO.

Hydro-sulphuret of Lithium may be prepared in the same way as the two former salts, and is left by evaporation as a crystalline solid. When heated in close vessels it parts with its water of crystallization, and like the two former salts retains its acid even at a red heat.

Hydro-sulphuret of Barium.—It is prepared by the action of hydrosulphuric acid on a solution of baryta with the precautions already mentioned for excluding atmospheric air, and crystallizes by evaporation in four-sided prisms, which are very soluble in water, but dissolve sparingly in alcohol. The crystals part with their water of crystallization when heated, and at a commencing red heat give out hydrosulphuric acid, leaving pure sulphuret of barium.

Hydro-sulphuret of Strontium is prepared like the former salt, and crystallizes in large radiated prisms, which when quite dry may be kept several days exposed to the air without change. When heated it loses its water and acid, and protosulphuret of strontium as a white powder is left.

Hydro-sulphuret of Calcium is formed in the same manner as the preceding salts; but it exists only in solution; for on attempting to crystallize by evaporation, hydrosulphuric acid is driven off, and the sulphuret of calcium in prisms of a silky lustre, is deposited. The hydro-sulphuret of magnesium likewise exists only in solution.

CARBO-SULPHURETS.

The acid of these sulphur-salts is bisulphuret of carbon; and the salts themselves are thus constituted:—

Names.	Sulphur.	Sulphur-acid.	Equiv.	Formulæ.
Carbo-sulphuret of Potassium . .	55·25 1 eq.+	38·32 1 eq.=	93·57	$KS+CS_2$.
Ditto Sodium . .	40·4 1 eq.+	38·32 1 eq.=	78·72	$NaS+CS_2$.
Ditto Lithium .	26·1 1 eq.+	38·32 1 eq.=	64·42	$LS+CS_2$.
Ditto Hydrosulphate of Ammonia .	34·25 1 eq.+	38·32 1 eq.=	72·57	$(H_3N+HS)+CS_2$. or $(NH_4,S)+CS_2$.
Ditto Barium . .	84·8 1 eq.+	38·32 1 eq.=	123·12	$BaS+CS_2$.
Ditto Strontium .	59·9 1 eq.+	38·32 1 eq.=	98·22	$SrS+CS_2$.
Ditto Calcium .	36·6 1 eq.+	38·32 1 eq.=	74·92	$CaS+CS_2$.
Ditto Magnesium .	28·8 1 eq.+	38·32 1 eq.=	67·12	$MgS+CS_2$.

Carbo-sulphuret of Potassium.—On agitating bisulphuret of carbon with a strong alcoholic solution of protosulphuret of potassium, the liquid when set at rest separates into three layers, the lowest of which is carbo-sulphuret of potassium, and is of the consistence of syrup. Another process is to digest bisulphuret of carbon at 86° in a corked bottle full of a strong aqueous solution of protosulphuret of potassium, until the latter is saturated. A concentrated solution of this salt is of a deep orange, almost red, colour; and when evaporated at 86° to the consistence of syrup, a deliquescent yellow crystalline salt is deposited, which is sparingly soluble in alcohol. On heating it to 150° it gives off water of crystallization; and when more strongly heated it is resolved into trisulphuret of potassium and charcoal.

Carbo-sulphuret of Sodium.—It is prepared like the former salts, and separates in yellow crystals from a very concentrated solution. It is deliquescent, and dissolves readily in alcohol as well as water.

The *Carbo-sulphuret of Lithium* resembles the preceding salt, and is very soluble in water and alcohol. Similar carbo-sulphurets are obtained by the action of solutions of sulphuret of barium, strontium, and calcium, on bisulphuret of carbon: the solutions are of an orange colour, and yield crystalline salts by evaporation.

Carbo-sulphuret of Hydrosulphate of Ammonia.—Zeise prepares this salt by filling a bottle with ten measures of nearly absolute alcohol saturated with ammoniacal gas and one measure of bisulphuret of carbon, and inserting a tight cork. As soon as the liquid has acquired a yellowish-brown colour, the bottle is plunged into ice-cold water, when the carbo-sulphuret is deposited either in yellow penniform crystals, or as a crystalline powder. The whole is thrown upon a linen filter, and the salt after being washed, first with absolute alcohol and then with ether, is dried by pressure within folds of bibulous paper. This salt is very volatile, passing off entirely at common temperatures, and can only be preserved in well-corked bottles. Exposed to the air it absorbs humidity and acquires a red colour. Its solution may be kept unchanged in bottles filled with it and tightly corked.

The carbo-sulphurets of barium, strontium, and calcium may be obtained by acting on bisulphuret of carbon with a solution of the protosulphurets of those metals. The resulting solutions are of an orange or brown colour, and the salts deposited by evaporation are of a citron-yellow when quite dry. The carbo-sulphuret of barium is of sparing solubility. The carbo-sulphuret of magnesium is best prepared by adding sulphate of magnesia to a solution of carbo-sulphuret of barium. Berzelius has also prepared several carbo-sulphurets of the metals of the second class.

ARSENIO-SULPHURETS.

Berzelius finds that each of the three sulphurets of arsenic is capable of acting as a sulphur-acid, giving rise to three distinct families of sulphur salts, distinguishable by the terms *arsenio-persulphurets*, *arsenio-tersulphurets*, and *arsenio-bisulphurets.*

Persulphuret of arsenic is a very powerful sulphur-acid, violently displacing hydrosulphuric acid from its combinations with sulphur-bases, even at common temperatures; and when digested with earthy or alkaline carbonates, it expels carbonic acid. The salts of this sulphur-acid may be prepared by several different methods:—

1. By digesting the persulphuret of arsenic in a solution of a sulphur-base, such as sulphuret of potassium or sodium, until it is saturated. The resulting soluble arsenio-persulphuret may be employed to prepare insoluble salts of the same sulphur-acid by means of double decomposition. If a persulphuret of potassium is used, sulphur is deposited.

2. By decomposing a hydrosulphuret of a sulphur-base with persulphuret of arsenic, in which case hydrosulphuric gas is disengaged with effervescence.

3. By decomposing a solution of an arseniate by means of hydrosulphuric acid or hydrosulphate of ammonia.

4. By dissolving persulphuret of arsenic in a solution of caustic alkali, such as potassa; when an interchange of elements between portions of the alkali and persulphuret ensues, whereby arsenic acid and protosulphuret of potassium are generated. In this case

1 eq. Persulphuret and 5 eq. Potassa yield 1 eq. Arsenic Acid and 5 eq. Protosulphuret.
AsS_5 $5KO$ AsO_5 $5KS$.

Two salts are thus generated and co-exist in the solution, namely, arseniate of potassa and arsenio-sulphuret of potassium. Similar changes invariably occur when sesquisulphuret of arsenic, sesquisulphuret of antimony, and other sulphur-acids are boiled with alkaline solutions: an oxy-salt, the acid of which is formed of oxygen and the electro-negative metal, is always generated; and this salt, if soluble in water, remains together with the sulphur-salts in solution. An alkaline carbonate may be substituted for a pure alkali, but then carbonic acid is expelled. These principles are concerned in the production of kermes, as already explained.

5. The last method which requires mention, is by exposing a mixture of persulphuret of arsenic and an alkaline carbonate to a red heat in a covered vessel. Carbonic acid gas is disengaged; and an interchange of elements, similar to that just explained, takes place between a portion of the alkali and the sulphuret. The fused mass, accordingly, contains an arseniate of the alkali, as well as a sulphur-salt. This tendency to the formation of a double sulphuret is the reason why, in decomposing orpiment by black flux, the whole of the arsenic is never sublimed: a part is uniformly retained in the form of a sulphur-salt, the arsenio-sesquisulphuret of sulphuret of potassium.

Most of the arsenio-persulphurets of the second class of metals are insoluble; but those of the metals of the alkalies and alkaline earths are very soluble in water, have a lemon-yellow colour in the anhydrous state, and are colourless when combined with water of crystallization or in solution. When exposed to heat in close vessels they give off sulphur, and an arsenio-sesquisulphuret is generated. In the solid state they are very permanent in the air, and even in solution oxidation takes place with great slowness. When decomposed by an acid, persulphuret of arsenic subsides, hydrosulphuric acid gas escapes, and a salt of the alkali is generated. Some chemists may doubt the possibility of the arsenio-persulphurets dissolving as such in water: they may consider the arsenic and the metal of the sulphur-base to be united with oxygen, and all the sulphur with hydrogen; but this supposition, if followed out, leads into such complex and improbable modes of combination, that I see no alternative but implicitly to admit the views here adopted.

The following table exhibits the composition of the principal arsenio-persulphurets:—

Names.	Sulph.-base.	Sulph.-acid.	Equiv.	Formulæ.
Triarse.-persulph. of Potassium .	165·75 3 eq.	+155·9 1 eq.	=321·65	$3KS+AsS_5$.
Diarse.-persulph. do.	110·5 2 eq.	+155·9 1 eq.	=266·4	$2KS+AsS_5$.
Arsenio-persulph. do.	55·25 1 eq.	+155·9 1 eq.	=211·15	$KS+AsS_5$.
Triarse-persulph. of Sodium . .	121·2 3 eq.	+155·9 1 eq.	=277·1	$3NaS+AsS_5$.
Do. in crystals with 270 or 30 eq. of water			=547·1	
Diarse -persulph. of Sodium . .	80·8 2 eq.	+155·9 1 eq.	=236·7	$2NaS+AsS_5$.
Arsenio-persulph. do.	40·4 1 eq.	+155·9 1 eq.	=196·3	$NaS+AsS_5$.
Triarse.-persulph. of Hydrosulphate of Ammonia .	102.75 3 eq.	+155·9 1 eq.	=258·65	$3(H_3N+HS)+AsS_5$.
Diarse.-persulph. do.	68·5 2 eq.	+155·9 1 eq.	=224·4	$2(H_3N+HS)+AsS_5$.
Arsenio-persulph. do.	34·25 1 eq.	+155·9 1 eq.	=190·15	$(H_3N+HS)+AsS_5$.

Arsenio-persulphurets of Potassium.—The diarsenio-persulphuret is best obtained by the action of hydrosulphuric acid gas on the diarseniate of potassa, and yields a colourless solution. By evaporation in vacuo it is reduced to a yellowish viscid mass which dries imperfectly, but when exposed for some time to the open air at length becomes a crystalline mass of a lemon-yellow colour, in which rhomboidal tables are perceptible. When this salt is mixed with alcohol, it is resolved into the triarsenio-persulphuret, which is insoluble in the alcohol, and the arsenio-persulphuret, which remains in solution. The latter has not been obtained in the solid state. The former is deliquescent and very soluble in water; but when its solution is gently evaporated, the residue has a radiated crystalline texture.

Arsenio-persulphurets of Sodium.—The diarsenio-persulphuret is formed like the corresponding salt of potassium, is very soluble in water, and by evaporation yields a lemon-yellow mass, which attracts humidity from the air. On mixing its solution with alcohol it is resolved into the arsenio-persulphuret and triarsenio-persulphuret of sodium, and the latter falls in scaly crystals of snowy whiteness, which may be collected on a filter, washed with alcohol, and dried without change. This salt by solution in water and evaporation may be obtained in rhomboidal tables or prisms derived from a rhombic prism. The crystals undergo no change in the air, and contain 30 eq. of water. The arsenio-persulphuret has been obtained only in solution. The *Arsenio-persulphurets of lithium* are very analogous to those of sodium.

Arsenio-persulphurets of hydrosulphate of Ammonia.—The diarsenio-persulphuret is obtained as a colourless solution by decomposing with hydrosulphuric acid gas a solution of triarseniate of oxide of ammonium and basic water. By spontaneous evaporation it becomes a viscid mass of a reddish-yellow colour, and which cannot be fully dried without decomposition. When its solution is mixed with hydrosulphate of ammonia and agitated with hot alcohol, the triarsenio-sulphuret is deposited in colourless prisms, which, after being well washed with alcohol and dried on bibulous paper, undergo no change by exposure to the air. The arsenio-persulphuret remains in the alcoholic solution.

Analogous salts may be similarly prepared with barium, strontium, calcium, and magnesium ; and insoluble compounds of the same nature may be formed by way of double decomposition by mixing soluble arsenio-persulphurets with oxy-salts of the second class of metals.

The salts in which tersulphuret of arsenic acts as an acid, resemble those of the persulphuret both in their general characters and mode of formation. Those formed with the bisulphuret of arsenic cannot be made in the moist way by direct union of their ingredients ; but when solutions of the arsenio-tersulphurets are evaporated, spontaneous decomposition takes place, the salts of protosulphuret of arsenic of a reddish-brown colour subside, while arsenio-persulphurets remain in solution.

MOLYBDO-SULPHURETS.

The electro-negative ingredient of these salts is the tersulphuret of molybdenum, and the most remarkable of them is the molybdosulphuret of potassium, which is readily formed by decomposing with hydrosulphuric acid gas a rather strong solution of molybdate of potassa. If no iron is present, the liquid acquires a beautiful red colour like the solution of bichromate of potassa, and on evaporation prismatic crystals with four and eight sides are deposited. Berzelius describes this compound as one of the most beautiful which chemistry can produce: the crystals, by transmitted light, are ruby-red, and their surfaces, while moist with the solution which yielded them, shine like the wings of certain insects with a metallic lustre of a rich green tint. The crystals are anhydrous, dissolve readily in water, but are insoluble in alcohol. On the addition of sulphuric or any of the stronger acids, a salt of potassa is generated with escape of hydrosulphuric acid, and precipitation of tersulphuret of molybdenum.

Soluble molybdo-sulphurets of sodium, lithium, and ammonia of a red colour, may be obtained by a process similar to that for preparing the preceding compound. The composition of these salts is as follows:—

Names.	Sulphur-base.	Sulphur-acid.	Equiv.	Formulæ.
Molybdo-sulphuret of Potassium .	55·25 1 eq.+	96·26 1 eq.=	151·51	$KS+MoS_3$.
Molybdo-sulphuret of Sodium .	40·4 1 eq.+	96·26 1 eq.=	136·66	$NaS+MoS_3$.
Molybdo-sulphuret of Lithium .	26 1 eq.+	96·26 1 eq.=	122·36	$LS+MoS_3$.
Molybdo-sulphuret of Hydrosulphate of Ammonia .	34·25 1 eq.+	96·26 1 eq.=	130·51	$(H_3N+HS)+MoS_3$.

Similarly constituted soluble salts of a red or orange colour may be obtained by boiling solutions of sulphuret of barium, strontium, and calcium with an excess of tersulphuret of molybdenum. The insoluble molybdo-sulphurets may be prepared from the former by way of double decomposition.

ANTIMONIO-SULPHURETS.

When two parts of carbonate of potassa are intimately mixed with four of sesquisulphuret of antimony and one part of sulphur, and the mixture is fused, an antimonio-persulphuret of potassium is generated. On digesting in water, a subantimonio-persulphuret is dissolved, and is deposited by gentle evaporation in large colourless tetrahedrons, which become yellow on exposure to the air. The salts which this sulphur-acid forms with other bases have not been examined.

A sulphur-salt of potassium, in which tersulphuret of antimony is the acid, remains in solution after the kermes is deposited, and may be obtained by evaporation in vacuo in colourless irregular crystals which deliquesce rapidly in the air.

TUNGSTO-SULPHURETS.

The best known of these salts is that of potassium, in which tersulphuret of tungsten is combined with protosulphuret of potassium. It is formed when a solution of tungstate of potassa is decomposed by hydrosulphuric acid, and crystallizes by evaporation in flat quadrilateral prisms. which are anhydrous, and are of a pale red colour. It dissolves sparingly in alcohol, but is freely soluble in water, yielding an orange-coloured solution. When mixed with a quantity of acid insufficient for entire decomposition, it forms a bitungsto-sulphuret of a brown colour.

The tungsto-sulphuret of potassium unites with tungstate of potassa as a double salt, which yields a yellow solution, and crystallizes in rectangular tables of a lemon-yellow colour. It combines also with nitrate of potassa, and the resulting double salt crystallizes in large transparent crystals of a ruby-red tint, and when heated detonates like gunpowder.

The tungsto-sulphuret of sodium is prepared from tungstate of soda by hydrosulphuric acid, and crystallizes with difficulty in irregular crystals of a red colour. It deliquesces in the air, and is soluble in water and alcohol.

SECTION IV.

CLASS OF SALTS. ORDER IV.

HALOID-SALTS.

In this section are included substances composed like the preceding salts of two bi-elementary compounds, one or both of which are analogous in composition to sea-salt. The principal groups consist of double chlorides, double iodides, and double fluorides. In these the haloid-bases belong usually to the electro-positive metals, and the haloid-acids to the metals which are electro-negative. I shall apply to them the same principle of nomenclature as to the sulphur-salts.

HYDRARGO-CHLORIDES.

The haloid-acid of this family is bichloride of mercury, which reddens litmus paper, and loses the property when a haloid-base is present, thus bearing a close analogy to ordinary acids. Its principal salts which have been examined are thus constituted :—

Names.	Basic Chloride.	Bichlor.	Merc.	Equiv.	Formulæ.
Dihydrargo-chloride of Potassium . .	149·14 2 eq.	+273·84	1 eq.	=422·98	$2KCl+HgCl_2$.
Do. in rhombic prisms with 18 or 2 eq. of water				=440·98	
Hydrargo-chloride of Potassium . .	74·57 1 eq.	+273·84	1 eq.	=348·41	$KCl+HgCl_2$.
Do. in acicular crystals with 18 or 2 eq. of water				=366·41	

Names.	Basic Chloride.	Bichlor.	Merc.	Equiv.	Formulæ.
Bihydrargo-chloride of Potassium . .	74·57	1 eq.+547·68	2 eq.	=622·25	$KCl+2HgCl_2$.
Do. in acicular crystals with 36 or 4 eq. of water				=658·25	
Hydrargo-chloride of Sodium . . .	59·72	1 eq.+273·84	1 eq.	=333·56	$NaCl+HgCl_2$.
Do. in crystals with 36 or 4 eq. of water . .				=369·56	
Dihydrargo-chloride of hydrochlo. of Ammonia	105·14	1 eq.+273·84	1 eq.	=378·98	$2(H_3N+HCl)$ $+HgCl_2$.
Do. in flat rhombic prisms with 18 or 2 eq. of water				=396·98	

The preceding salts, except the last, were first prepared and examined by Bonsdorff (An. de Ch. et Ph. xliv. 189); and they are obtained by mixing the ingredients in the ratio for combining, and setting aside the solution to crystallize. The ammoniacal salt has long been known under the name of *salt of alembroth*. Bonsdorff obtained similar compounds with the chlorides of lithium, barium, strontium, calcium, magnesium, manganese, iron, cobalt, nickel, and copper. Those of lithium, calcium, magnesium, and zinc are deliquescent. The hydrargo-chlorides of iron and manganese are isomorphous, and crystallize in rhombic prisms. Hydrochloric acid combines with bichloride of mercury, and yields a very soluble salt, which may be obtained in crystals; the electro-positive ingredient is here probably hydrochloric acid, and as such will be considered as chloride of hydrogen, with properties analogous to the chlorides of electro-positive metals.

AURO-CHLORIDES.

These salts, the electro-negative ingredient of which is the terchloride of gold, have been studied by Berzelius, Johnston, and Bonsdorff. They are prepared by mixing the chlorides in atomic proportions, and setting aside the solution to crystallize.

Most of them have an orange or yellow colour, and consist of single equivalents of their constituent chlorides, as is exemplified by the composition of the three following salts:—

Names.	Basic Chlorides.	Terch. Gold.	Equiv.	Formulæ.
Auro-chloride of Potassium . . .	74·57	1 eq.+305·46	1 eq.=380·03	$KCl+AuCl_3$.
Do. in prisms with 45 or 5 eq. of water .			=425·03	
Auro-chloride of Sodium	59·72	1 eq.+305·46	1 eq.=365·18	$NaCl+AuCl_3$.
Do. in 4-sided prisms with 36 or 4 eq. of water			=401·18	
Auro-chloride of hydrochlorate of Ammonia	105·14	1 eq.+305·46	1 eq.=410·60	(H_3N+HCl) $AuCl_3$.
Do. in acicular crystals with 36 or 4 eq. of water			=446·6	

Auro-chloride of Potassium.—This salt crystallizes either in striated prisms or thin hexagonal tables, which effloresce in a dry air, and lose all their water at 212°. At a red heat, the terchloride of gold is decomposed, leaving chloride of potassium and metallic gold. This salt is soluble both in water and alcohol.

Auro-chloride of Sodium crystallizes in long quadrilateral prisms, which may be exposed to the air without change, and fuse readily in their water of crystallization. The *auro-chloride of lithium* is deliquescent.

Auro-chloride of Hydrochlorate of Ammonia.—It crystallizes in transparent needles or small prisms, which become opaque by exposure to the air, and are soluble in water and alcohol.

Auro-chloride of Hydrogen.—In this compound hydrochloric acid is probably the positive chloride. It crystallizes readily in long acicular crystals of a light yellow colour when an acid solution of gold is cautiously evaporated. The crystal undergo no change in dry air, but in a moist atmosphere deliquesce into a yellow liquid.

Bonsdorff has prepared the auro-chlorides of barium, strontium, calcium, magnesium, manganese, zinc, cadmium, cobalt, and nickel. Most of them crystallize in prisms, and contain water of crystallization.

PLATINO-CHLORIDES.

Both the protochloride and bichloride of platinum act as haloid-acids. Magnus prepared the platino-protochloride of potassium by mixing chloride of potassium with a solution of protochloride of platinum in hydrochloric acid. It crystallizes by evaporation in red, anhydrous, 4-sided prisms, which are insoluble in alcohol, but dissolve readily in water. It consists of single equivalents of its constituent chlorides.

The *platino-protochloride of sodium* may also be prepared, is soluble in water and alcohol, and crystallizes with difficulty. A similar salt may be formed with hydrochlorate of ammonia, and is isomorphous with that of potassium, which it also resembles in its properties, comsition, and mode of preparation.

The solution of protochloride of platinum in hydrochloric acid, which has a deep red tint, is doubtless a double chloride, but it has not been obtained in crystals.

The principal salts of bichloride of platinum are those of potassium, sodium, and ammonium, which are thus constituted:—

Names.	Basic Chlorides.	Bichl. of Plat.	Equiv.	Formulæ.
Platino-bichloride of Potassium . .	74·57 1 eq.	+169·64 1 eq.	=244·21	$KCl+PtCl_2$.
———— Sodium	59·72 1 eq.	+169·64 1 eq.	=229·36	$NaCl+PtCl_2$.
Do. in prisms with 54 or 6 eq. of water . .			=283·36	
Platino-bichloride of hydrochlorate of Ammonia	105·14 1 eq.	+169·64 1 eq.	=274·78	$(H_3N+HCl)+PtCl_2$ or $(NH_4, Cl)+PtCl_2$.

Platino-bichloride of Potassium.—The production of this salt by mixing its constituents in solution, constitutes one of the best tests for potassa. It is commonly obtained as a powder, of a pale lemon-yellow colour; but by slow evaporation it yields small octohedrons of a brilliant lustre. It is anhydrous, insoluble in alcohol, and is sparingly dissolved by cold, but more freely by hot water. Heated to redness it yields chlorine, and the residue consists of platinum and chloride of potassium.

Platino-bichloride of Sodium.—This salt crystallizes in fine transparent prisms of a deep yellow colour, which are soluble in water and alcohol. When gently heated it loses its water of crystallization, and becomes a pale yellow powder.

Platino-bichloride of Hydrochloride of Ammonia falls as a lemon-yellow powder when sal-ammoniac is mixed with a strong solution of bichloride of platinum. It resembles the double salt of potassium in its properties and form, crystallizing in small anhydrous octohedrons when its aqueous solution is slowly evaporated. Its constitution, when viewed as a compound of ammonium, is also analogous to that of the potassium salt. It is then $(NH_4,Cl) + Pt,Cl_2$. This salt is employed in the preparation of platinum, and when heated to redness leaves that metal in a spongy state.

Bonsdorff has prepared the platino-bichlorides of barium, strontium, calcium, and several other metals. Most of them crystallize with water of crystallization, and have a yellow or orange colour.

PALLADIO-CHLORIDES.

Both of the chlorides of palladium act as haloid-acids, combining with many of the metallic chlorides, when their respective solutions are mixed and evaporated. The principal ones which have been examined are those with potassium, sodium, and ammonia, which consist of single equivalents of their ingredients.

The palladio-protochloride of potassium crystallizes in four-sided prisms of a dirty yellow colour, which are anhydrous, insoluble in alcohol, and freely soluble in water. The corresponding salt of sodium is deliquescent and soluble both in water and alcohol. That of hydrochlorate of ammonia is isomorphous with the salt of potassium, which it resembles in its other properties.

The palladio-bichloride of potassium is obtained by evaporating the palladio-protochloride with nitro-hydrochloric acid, when microscopic crystals of a cinnabar-red colour are deposited, which by a glass are found to be regular octohedrons, analogous in form and constitution to the corresponding salt of platinum. It is anhydrous, insoluble in alcohol, and nearly so in water. When heated, or by continued ebullition, it is reconverted into the palladio-protochloride of potassium. The corresponding salt of hydrochlorate of ammonia is obtained in a similar manner, and resembles the former in form and other properties.

RHODIO-CHLORIDES.

The sesquichloride of rhodium combines with the chlorides of potassium and sodium, and the resulting salts are thus constituted :—

Names.	Basic Chlor.	Sesquichl.	Rhod.	Equiv.	Formulæ.
Dirhodio-chloride of Potassium	149·14 2 eq.	+210·66	1 eq.	=359·80	$2KCl+R_2Cl_3$.
Do. in four-sided prisms with 18 or 2 eq. of water				=277·8	
Trirhodio-chloride of Sodium	179·16 3 eq.	+210·66	1 eq.	=389·82	$3NaCl+R_2Cl_3$.
Do. in prisms with 162 or 18 eq. of water .				=551·82.	

Dirhodio-chloride of Potassium.—It is obtained by mixing the respective chlorides in the ratio above assigned, and crystallizes in four-sided rectangular prisms, which are of a deep red colour, insoluble in alcohol, and contain 18 parts or 2 eq. of water combined with 359·8 parts or 1 eq. of the salt.

Hydrochlorate of ammonia yields a similar double salt, analogous in its properties to the preceding.

Trirhodio-chloride of Sodium.—This salt crystallizes in large prismatic crystals of a deep red colour, which lose part of their water in a dry air, and become covered with a red powder. They are insoluble in alcohol.

IRIDIO-CHLORIDES.

The chlorides of iridium act as haloid-acids. The most remarkable of its salts is the iridio-bichloride of potassium, which in form and properties resembles the platino-bichloride of potassium, crystallizing in brilliant octohedrons, but of a black colour, which are sparingly soluble in water. Hydrochlorate of ammonia forms with it a similar salt, which is of a deep cherry-red colour.

OSMIO-CHLORIDES.

Berzelius has described the osmio-bichloride of potassium, which resembles in form, composition, and most of its properties, the corresponding salts of platinium and iridium. It is insoluble in alcohol, and but sparingly dissolved in water; but its aqueous solution, when gently evaporated, yields octohedral crystals of a deep brown colour.

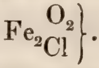
OXY-CHLORIDES.

Chemists are acquainted with a considerable number of compounds in which a metallic oxide is united with a chloride either of the same metal, which is the most frequent, or of some other chloride. These compounds are commonly termed *sub-muriates*, on the supposition that they consist of hydrochloric acid combined with two or more eq. of an oxide.

Oxy-chlorides of Iron.—When the crystallized protochloride of iron is heated without exposure to the air, the last portions of its water exchange elements with part of the chloride of iron, yielding hydrochloric acid, which is evolved, and protoxide of iron. On raising the heat so as to expel the pure chloride of iron, a deep green oxy-chloride in scaly crystals remains. (Berzelius.)

The ochreous matter which falls when a solution of the proto-chloride of iron is exposed to the air, is hydrated peroxide of iron combined with some perchloride. A similar hydrate is obtained by mixing with a solution of the perchloride of iron a quantity of alkali insufficient for complete decomposition. When a solution of the perchloride is evaporated to dryness without exposure to the air, the last portions of water exchange elements with the perchloride, hydrochloric acid is disengaged, and after subliming the pure anhydrous perchloride, a compound in large, brown, shining laminæ is left, which consists of peroxide and perchloride of iron. (Berzelius.)

Mr. Phillips has described a soluble oxy-chloride which appears to consist of 1 eq. of perchloride of iron with 9 eq. of the peroxide. It is prepared by digesting hydrochloric acid with the required proportion of the moist hydrated peroxide. The solution is of a brownish-red colour, and a precipitate is occasioned either by a little more of the peroxide or a little acid, indicating the formation of other oxy-chlorides which are insoluble. (Phil. Mag. and An. viii. 406.)

By adding bleaching-liquor to protonitrate of iron, Millon obtained an oxychloride, corresponding to the sesquioxide, which it resembles in appearance. Its formula is  $Fe_2\left.\begin{matrix}O_2\\Cl\end{matrix}\right\}$.

Oxy-chlorides of Tin.—When a large quantity of water is poured on crystallized protochloride of tin, a portion of water and protochloride exchange elements, an acid solution is formed, containing the double chloride of tin and hydrogen, and a white powder subsides, which is a compound of the protoxide and protochloride of tin.

Oxy-chloride of Chromium.—This compound, which was long considered as the terchloride, was first shewn to be an oxy-chloride by Rose. It has already been mentioned.

Oxy-chloride of Tungsten.—This compound, the nature of which was first pointed out by Rose, has already been described.

Oxy-chloride of Molybdenum.—Formerly described as the terchloride, but shewn by Rose to be really similar in constitution to the two preceding compounds.

Oxy-chloride of Antimony.—It falls as a white curdy precipitate when sesquichloride of antimony is thrown into water, and, according to an analysis by Phillips, contains about 7·8 per cent. of chlorine.

Oxy-chloride of Cerium.—This compound is generated by heating the hydrated protochloride, just as when the protochloride of iron is distilled.

Oxy-chloride of Bismuth.—It is prepared by pouring a neutral solution of nitrate of oxide of bismuth into a concentrated solution of sea-salt; and a similar compound, but with more oxide, is formed when a dilute solution of sea-salt is used. They are both heavy insoluble powders of a very white colour.

Oxy-chloride of Copper.—This compound falls as a green hydrate when potassa is added to a solution of chloride of copper in quantity insufficient for its complete decomposition. When its water is expelled it becomes of a liver-brown colour. Berzelius states it to consist of 1 eq. of the chloride and 3 eq. of oxide of copper. It is used as a pigment under the name of *Brunswick green*, being prepared for that purpose by exposing metallic copper to hydrochloric acid or a solution of sal-ammoniac. The same compound is generated during the corrosion of copper in sea-water. Millon, by the process above mentioned, obtained an oxy-chloride of copper, $\mathrm{Cu_2}\left.\begin{matrix}\mathrm{O}\\ \mathrm{Cl}\end{matrix}\right\}$, which seems to be a basic compound.

Oxy-chlorides of Lead.—A compound of 1 eq. protochloride to 2 eq. of protoxide of lead has been found as a colourless mineral. Another oxy-chloride with 3 eq. of the protoxide is prepared by adding pure ammonia to a hot solution of chloride of lead. It falls as a heavy white hydrate; but on expelling its water by heat, it acquires a pale yellow colour. A third oxy-chloride with a still larger proportion of oxide is used as a pigment under the name of *mineral* or *patent yellow*; and it is prepared by the action of moist sea-salt on litharge, by which means portions of the protoxide and sea-salt exchange elements, yielding soda and chloride of lead. After washing away the alkali, the mixed oxide and chloride are dried and fused. Millon states that bleaching liquor, added to nitrate of lead, throws down a white precipitate, which soon becomes brown. These colours indicate different mechanical states of the same compound, $\mathrm{Pb}\left.\begin{matrix}\mathrm{O}\\\mathrm{Cl}\end{matrix}\right\}$; that is an oxychloride, corresponding to the peroxide, $\mathrm{Pb}\left.\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\}$.

Oxy-chloride of Mercury.—This compound is obtained as a shining crystalline powder, of a brownish-black colour, when peroxide of mercury is boiled with a solution of the bichloride. It is anhydrous, and consists of single equivalents of the oxide and chloride. Formula, $\mathrm{HgO_2}$ or $\mathrm{Hg}\left.\begin{matrix}\mathrm{O}\\\mathrm{Cl}\end{matrix}\right\}$.

Millon's experiments alluded to above, and in the section on the hypochlorites, if confirmed, will add the bleaching compounds to the order of oxy-chlorides; and will render it probable that oxy-chlorides in general are not compounds of oxides and chlorides, but compounds of the metal with oxygen and chlorine corresponding to the peroxide of the respective metals. But the experiments of Millon are not perfectly satisfactory on this point, and we must consider the subject as open to investigation.

CHLORIDES WITH AMMONIA.

Several interesting compounds of chlorides with ammonia have been studied by Persoz and Rose. (An. de Ch. et Ph. xliv. 315, and li. 5, and Pog. Annalen, xx. 149.) The perchlorides of tin, titanium, antimony and iron, and the oxy-chloride of chromium, absorb ammonia at common temperatures; and most of the other chlorides absorb it when gently warmed. The chlorides of potassium, sodium, and barium do not absorb ammonia; while those of strontium and calcium combine with 4 eq. of the alkali. Chloride of copper absorbs 3 eq. and acquires the same deep blue tint as the armoniaco-sulphate of copper. Chloride of nickel unites with 3, and chloride of cobalt with 2 eq. of ammonia. Chloride of silver takes up slowly 1½ eq. Calomel absorbs half an eq. and forms a black compound; but on exposure to the air the ammonia flies off, and pure white calomel remains. Corrosive sublimate, by the aid of heat, rapidly absorbs half an eq. of ammonia, and forms a white compound, which is insoluble in water, and bears a considerable temperature without decomposition: the white precipitate of pharmacy is probably analogous in nature, though the ratio of its ingredients is different. Perchloride of titanium combines with 2 eq. and that of tin with 1. The bromides and iodides, as well as the bicyanuret of mercury, absorb ammonia in the same manner as the chlorides. Nearly all of these compounds depend on very feeble affinities. Most of them lose their ammonia by mere exposure to the air, and it is expelled from nearly all by a very moderate heat; in some, as with perchloride of titanium, heat occasions reactions between the chlorine and ammonia, and the metal is insulated; but in general the alkali is simply expelled, and the chloride returns to its former condition. Though these ammoniacal chlorides may be viewed as salts in which a metallic chloride acts as an acid, they appear to be more closely allied to those singular compounds of ammonia with the oxy-salts which have already been noticed. To this remark some of them, of which the ammoniacal chloride of mercury is an instance, are probably exceptions, and are rather, as Kane has shewn, to be viewed as compounds of amide. They will be referred to in this form in the organic chemistry.

CHLORIDES WITH PHOSPHURETTED HYDROGEN.

The analogy which Rose has traced between ammonia and phosphuretted hydrogen is especially remarkable in the compounds which they both form with metallic chlorides. He has examined the compounds of phosphuretted hydrogen with the perchlorides of titanium, tin, antimony, iron, and alumina, all of which correspond to ammoniacal chlorides of similar composition. The phosphuretted hydrogen is in all readily displaced by water, or a solution of ammonia. Rose observed that the resulting compound is the same in character and composition whichever of the two kinds of phosphuretted hydrogen were used in its preparation. He also found that the gas, when displaced from perchloride of titanium by water, does not inflame spontaneously; whereas, if displaced by a solution of potassa or its carbonate, by carbonate of ammonia or hydrochloric acid, the gas is spontaneously inflammable. He was thus able to disengage at will either variety of phosphuretted hydrogen from the same compound, without reference to the kind which had been used in its preparation. These facts first led Rose to the opinion that the two gases of phosphorus and hydrogen must be identical in composition; but we now know that the spontaneous combustibility depends on the presence of a small proportion of the vapour of a liquid phosphuretted hydrogen, which is in a high degree spontaneously inflammable, but is liable to spontaneous decomposition, losing that property.

DOUBLE IODIDES.

These compounds have not yet been closely studied; but there is no doubt that the iodides are capable of forming with each other an extensive series of compounds. Bonsdorff obtained the hydrargo-biniodide of potassium by saturating a strong solution of iodide of potassium with biniodide of mercury: it may also be formed by dissolving corrosive sublimate in a solution of iodide of potassium, evaporating to dryness, and digesting in alcohol, when the double iodide is dissolved, and chloride of potassium is left. A variety of double iodides have been described by Boullay, and among them a compound of biniodide of mercury and hydriodic acid. (An. de Ch. et Ph. xxxiv.) In general the double hydrargo-biniodides contain single equivalents of the respective iodides. Liebig obtained a compound of the bichloride and biniodide of mercury, consisting of 2 eq. of the former to 1 eq. of the latter, as indicated by the formula $HgI_2 + 2HgCl_2$.

Several compounds of biniodide of platinum with other iodides have been studied by Kane and Lassaigne. (Dublin Journal of Science, i. 304, and An. de Ch. et Ph. li. 125.) The compounds at present known are thus constituted:—

Names.	Basic Iod.	Biniod. Plat.	Equiv.	Formulæ.
Platino-biniodide of Potassium	165·45 1 eq.	+351·4 1 eq.	=516·85	$KI+PtI_2$.
Do. of Sodium . . .	150·6 1 eq.	+351·4 1 eq.	=502·0	$NaI+PtI_2$.
Do. of Hydriodate of Ammonia	144·45 1 eq.	+351·4 1 eq.	=495·85	NH_4I+PtI_2.
Do. of Barium . . .	195 1 eq.	+351·4 1 eq.	=546·4	$BaI+PtI_2$.
Do. of Zinc	158·6 1 eq.	+351·4 1 eq.	=510·0	$ZnI+PtI_2$.
Do. of Hydrogen . . .	127·3 1 eq.	+351·4 1 eq.	=478·7	$HI+PtI_2$.

The platino-biniodide of potassium is prepared by digesting an excess of biniodide of platinum in a rather concentrated solution of iodide of potassium. By spontaneous evaporation it crystallizes in small rectangular plates surmounted sometimes with a four-sided pyramid, which are anhydrous, unchanged in the air, and insoluble in alcohol. The colour of the crystals is black with a metallic lustre, and they yield a deep claret-coloured solution with water. The biniodide of platinum appears to combine also with the iodide of platinum; but the compound has only been obtained in solution.

The platino-biniodides of sodium, barium, and zinc are obtained in the same manner as that of potassium, crystallize with difficulty, are deliquescent in the air, and dissolve in water and alcohol. The ammoniacal salt is analogous in its properties to that of potassium, with which it appears also to be isomorphous.

Platino-biniodide of Hydrogen.—This compound consists of hydriodic acid and biniodide of platinum, in which the former is regarded as the electro-positive element. It is prepared by acting on biniodide of platinum with a cold dilute solution of hydriodic acid, which gradually acquires a deep claret colour, and by evaporation under a bell-jar with quicklime, deposits black acicular crystals. The crystals become moist by exposure to the air.

Oxy-iodides.—The principal oxy-iodides at present known to chemists are those formed by the oxide and iodide of lead. When iodide of potassium is mixed with acetate of oxide of lead in excess, the yellow chloride at first formed combines with oxide of lead and acquires a white colour; and the same compound is obtained directly by employing a subacetate. Denot finds that there are three oxy-iodides, in which 1 eq. of iodide of lead is united with 1, 2, and 5 eq. of oxide of lead.

DOUBLE BROMIDES.

These compounds have not yet been studied; but Bonsdorff has proved the possibility of forming compounds similar in composition and properties to the double chlorides. He obtained the hydrargo-bibromide of potassium in crystals, consisting of 1 eq. of each bromide united with 2 eq. of water.

DOUBLE FLUORIDES.

The researches of Berzelius have led to the formation of several extensive families of double fluorides, in which the fluorides of boron, silicon, titanium, and of other electro-negative metals are the acids, and the fluorides of electro-positive metals are bases. In some instances hydrofluoric acid is a haloid-acid; but more commonly it acts the part of a base.

Hydro-fluorides.—In this family hydrofluoric acid is combined with the fluorides of electro-positive metals. If an equivalent of any electro-positive metal be indicated by M, then the general formula for this family is $MF + HF$.

The hydro-fluoride of potassium is made by mixing hydro-fluoric acid with a solution of fluoride of potassium, and evaporating by a gentle heat in a platinum capsule. It commonly crystallizes in confused laminæ; but by slow evaporation in square tables or cubes, which are anhydrous and dissolve freely in pure water. It fuses readily when heated, and loses all its hydrofluoric acid at a low red heat.

The hydro-fluoride of sodium is prepared as the preceding salt, and by spontaneous evaporation yields anhydrous rhombohedral crystals. It is sparingly soluble in cold, but much more freely in hot water.

The hydro-fluoride of lithium is also of sparing solubility. The fluorides of barium, strontium, calcium, and magnesium do not combine with hydrofluoric acid.

BORO-FLUORIDES.

When the terfluoride of boron (fluoboric acid gas) is acted upon by water, one out of every four eq. of the gas interchanges elements with water, giving rise to hydrofluoric and boracic acids, the former of which combines as a haloid-base with undecomposed terfluoride of boron, constituting the boro-hydrofluoric acid, but which may be viewed as the *boro-fluoride of hydrogen.* This change is such that

4 eq. Terfluoride of Boron	$4BF_3$	yield	3 eq. Terfluoride of Boron .	$3BF_3$.
			3 eq. Hydrofluoric Acid .	3HF.
and 3 eq. of water . .	3HO		and 1 eq. Boracic Acid .	BO_3.

By careful concentration and cooling, the boracic acid separates as a crystalline powder, and the boro-fluoride of hydrogen remains in solution. It is strongly acid to test paper, and its composition is indicated by the formula $HF + BF_3$, being an eq. of each fluoride. On adding potassa to this compound, it interchanges elements with hydrofluoric acid, and there results the boro-fluoride of potassium, $KF + BF_3$, the hydrogen being simply displaced by potassium. The protoxides of most other metals act precisely like potassa, and therefore the general formula of these compounds is $MF + BF_3$. When exposed to a strong heat, they all give off terfluoride of boron, and a metallic fluoride is left.

Boro-fluoride of Potassium.—It is prepared by dropping boro-fluoride of hydrogen drop by drop into a solution of a salt of potassa, and falls as a gelatinous transparent hydrate, which is a white very fine powder when dried. It has a slightly bitter taste, and is quite neutral to test paper, is very sparingly soluble in alcohol and cold water, but is dissolved freely by hot water, and subsides on cooling in small brilliant anhydrous crystals. At a strong red heat it gives off the terfluoride of boron, and fluoride of potassium remains.

The *boro-fluoride of sodium* is very soluble in water, and is therefore best obtained by the direct action of boro-fluoride of hydrogen on fluoride of sodium. It crystallizes by slow evaporation in large rectangular prisms, which redden litmus paper strongly. The boro-fluoride of lithium also crystallizes in large prisms, is very soluble in water, and deliquesces in the air.

The *boro-fluoride of barium* is prepared by adding carbonate of baryta to boro-fluoride of hydrogen till it ceases to be dissolved, avoiding any further addition. On evaporating to the consistence of a syrup long acicular crystals form, and by keeping the solution in a warm place it yields flat, four-sided, rectangular prisms. It is acid to test paper, and deliquescent. The boro-fluorides of calcium and magnesium may be prepared in a similar manner, and are soluble in water. Lead forms a soluble boro-fluoride, which crystallizes in the same manner as the boro-fluoride of barium.

SILICO-FLUORIDES.

The acid solution, called *silico-hydrofluoric acid*, may be viewed as the *subsesqui-silico-fluoride of hydrogen*, a compound of 157·16 parts or 2 eq. of fluoride of silicon and 59·04 or 3 eq. of fluoride of hydrogen (hydrofluoric acid), as indicated by the formula $3HF + 2SiF_3$. When the solution is neutralized with potassa, the alkali interchanges elements with the fluoride of hydrogen, water and fluoride of potassium are generated, and the latter combines with the fluoride of silicon. This double fluoride consists, therefore, of 157·16 parts or 2 eq. of fluoride of silicon, and 173·49 or 3 eq. of fluoride of potassium, the formula of which is $3KF + 2SiF_3$. A similar change ensues with the protoxides of most other metals, and hence the general formula of the silico-fluorides is $3MF + 2SiF_3$. On exposing these compounds to a red heat fluoride of silicon is disengaged.

Silico-fluoride of Potassium.—This salt falls as a semi-transparent jelly, which has the property of reflecting the colours of the rainbow; but when collected on a filter and dried, it becomes a dense white powder. By evaporating a saturated aqueous solution, it separates in minute anhydrous crystals. It is sparingly soluble in hot water, and still less so in cold water.

The *silico-fluoride of sodium* resembles the former salt, but is much more soluble in hot water. By evaporation it is obtained in minute anhydrous hexagonal prisms. The silico-fluoride of lithium forms similar crystals, but is more soluble in water.

The *silico-fluoride of barium* gradually falls in microscopic crystals, which through a glass appear as elongated prisms, when chloride of barium is mixed with the silico-fluoride of hydrogen, hydrochloric acid remaining in solution. This salt is very sparingly soluble in water, whether hot or cold.

The silico-fluorides of strontium, calcium, magnesium, and lead are best prepared by dissolving their respective carbonates in silico-fluoride of hydrogen. The salt of strontium crystallizes in short quadrilateral prisms, which lose their water of crystallization at a gentle heat and become opaque. For complete solubility in water they require a slight excess of hydrofluoric acid to be present, and then they dissolve freely. The salt of calcium crystallizes in regular quadrilateral prisms. It dissolves readily in water acidulated with hydrofluoric or hydrochloric acids, but is decomposed by pure water, yielding an acid soluble salt, and an insoluble sub-salt. The salts of magnesium and lead are very soluble, and leave a gummy mass by evaporation.

The silico-fluorides of manganese, iron, zinc, cobalt, nickel, and copper are soluble in water, and crystallize in similar hexagonal prisms, probably isomorphous, which contain respectively 1 eq. of the silico-fluoride and 7 eq. of water of crystallization.

TITANO-FLUORIDES.

Hydrofluoric acid dissolves titanic acid, and forms with it an acid solution which may be viewed as the titano-fluoride of hydrogen, consisting of 61·66 parts or 1 eq. of bifluoride of titanium, and 19·68 or 1 eq. of fluoride of hydrogen, expressed by the formula $HF + TiF_2$. When mixed with potassa, water and fluoride of potassium are generated, and the titano-fluoride of potassium results, the formula of which is $KF + TiF_2$. By substituting most other protoxides for potassa similar salts may be prepared, the general formula being $MF + TiF_2$.

Few of the titano-fluorides have as yet been studied. That of potassium crystallizes by evaporation in scales like boracic acid, which are anhydrous, and but sparingly soluble in cold water. The titano-fluoride of sodium is very soluble, and crystallizes with difficulty.

Similar double fluorides may be formed, in which the fluorides of molybdenum, tellurium, and platinum act as the electro-negative ingredients. Few of them, however, have as yet been studied. Berzelius has prepared the alumino-fluorides of potassium and sodium, and the zircono-fluoride of potassium. He employed the latter in the preparation of metallic zirconium. The alumino-fluoride of sodium is found in nature as a rare mineral called *cryolite.*

OXY-FLUORIDES.

Several fluorides combine with oxides in the same manner as chlorides and iodides. An oxy-fluoride of aluminium is prepared as an insoluble gelatinous hydrate by digesting hydrate of alumina in a solution of the sesquifluoride of aluminium. This oxy-fluoride, combined with silicate of alumina, constitutes the topaz. The neutral fluorides of cobalt, nickel, and copper are decomposed by hot water, being resolved into soluble hydro-fluorides and insoluble oxy-fluorides. Several other fluorides doubtless undergo a similar change. The oxy-fluoride of lead is generated either by digesting fluoride of lead in solution of ammonia, or by fusing together the fluoride and oxide of lead. It is more soluble than the fluoride, and the solution by exposure to the air gives a precipitate of carbonate of oxide of lead. The fluoride of lead also combines by fusion with chloride of lead. Fluoride of calcium forms a very fusible compound with sulphate of lime.

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